Volume XXV. *November, 1907.* *Number 5*

THE

PHYSICAL REVIEW.

THE DISCHARGE OF ELECTRICITY FROM POINTED CONDUCTORS DIFFERING IN SIZE.

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1. The discharge of electricity from a pointed conductor is dependent in a large measure upon the shape and size of the point used. In the investigation to be described a study is made of the effect of these qualities upon the current flowing to a plate from a variety of charged points. Incidentally, the effect of moderate changes of pressure and temperature upon the discharge is also considered.

To enable experimental results to be compared with any proposed mathematical analysis of the mechanism of the discharge from points, it is essential that these results be obtained under conditions that can be completely stated and so permit of exact duplication. Such is not the case with the results of previous experimenters on this subject, because the shapes and sizes of the points used are not given, and in some cases the effects are complicated by the presence of insulators and by the special form of the apparatus used.

Chattock,[1] however, found the electric force necessary to start a discharge by measuring the pull on the ends of steel needles having hemispherical ends of different diameters, the needles being connected to earth and placed at various distances from a charged plate. The electric intensity for any point was found to be independent of the distance between the plate and the point, and within certain limits the product of the force by the eight tenths power of the radius of the points was a constant.

[1] Phil. Mag. (5), 32, p. 285, 1891.

Precht[1] measured the potentials required to start a discharge from various sized points when these were directed towards the ceiling of the room, but he found no relation between the potentials and the size of the points.

2. In the experiments to be described in this paper the points used were cylinders of various diameters with their ends either hemispherical or plane. Such points are sufficiently described by simply stating the diameter of the cylinder, and they can be easily duplicated.

The arrangement of the apparatus was such as to give the most simple conditions possible for a point opposite a plane.

The potential required to start a discharge as well as the currents obtained with different potentials was measured in each case.

The subject matter will be treated under the following subdivisions:

(*a*) Description of apparatus ..... § 3
(*b*) Tests of apparatus ..... § 4
(*c*) Difficulties and irregularities ..... §§ 5, 6
(*d*) Procedure in experiments ..... § 7
(*e*) Positive discharge from points with hemispherical ends. Distance = 1.5 cm ..... §§ 8, 9
(*f*) Relation between current, voltage, minimum potential, and diameter of points ..... §§ 10, 11
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DESCRIPTION OF APPARATUS.

3. Since the discharge from points is affected by moisture in the air, it is necessary to place the point and plane in a closed vessel,

[1] Wied. Annal., 49, p. 166, 1893.

to permit the use of dry air. Attempts to use glass vessels of diameters up to 12 cm. proved unsatisfactory[1] because the results obtained with them were not the same as in the open air. Since the current is altered by touching the glass vessel during the discharge, it appears that the glass surface becomes charged sufficiently to affect the potential gradient between the point and plane.

The apparatus finally adopted is shown in diagram in Fig. 1.

The point and plane were inclosed in the brass cylindrical vessel *R*, which was 15 cm. high and 13 cm. in diameter. The plane was a flat, polished, brass disc *O*, 7.5 cm. in diameter. It was supported by the hard rubber post *P*, and the current flowing to it was conducted by means of the rod *Q* and its attached wires to the D'Arsonval galvanometer *G* and its shunt *S*, whence it passed through the telephone receiver *T* to earth.

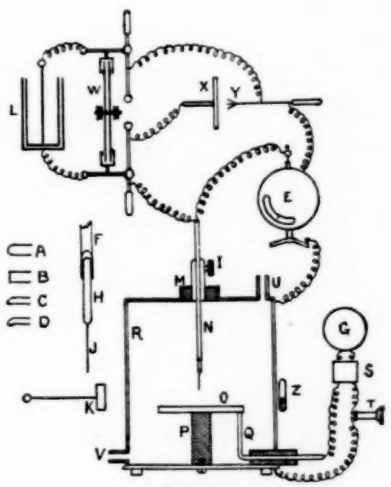

Fig. 1.

The brass rod *N* which carried the points was movable in a metal sleeve, to which it could be fastened by means of the screw *I*. It was insulated from the vessel by the large sulphur plug *M*. The manner in which the points were supported so as to be readily interchangeable, is shown enlarged by *JHF*.

The points *J* were cylindrical wires, for the most part of brass. They were about 1.5 cm. long and were soldered to the holders *H* which were about 3 mm. in diameter. These holders could easily be slipped into the opening *F* at the end of the rod *N*, and were held there by friction.

There was an opening, with a removable cover, in the side of the vessel *R*, which is not shown in the figure. Through this the distance between the point and the plane was adjusted by the aid of the gauge *K*, which consisted of a brass cylinder of a definite

[1] Compare F. Tamm, Annal. der Phys. (4), 6, p. 269, 1901.

height carrying a small handle. Placing this gauge on the plate *O*, the height of the point was brought accurately to the level of the top of the gauge and then clamped in place by the screw *I*.

The electricity was supplied to the points by a small Wimshurst machine *W* which was run by a motor. A battery of nine large Leyden jars, represented by *L*, was placed in parallel with the poles of the machine. This served to maintain a very constant voltage as any irregularities in the generation of electricity by the machine had a negligible effect upon the large capacity of the system. The magnitude of the voltage obtained was regulated by changing the speed of the motor and by altering the distance between the auxiliary point and plane *XY*, of which the point was always kept negative. For small currents with voltages below 2,000 it was sometimes found necessary simply to turn the machine very slowly by hand.

The potentials were measured by the Braun voltmeter *E*, reading to 10,000 volts. This was tested by comparing it with a Kelvin vertical electrostatic voltmeter having a range from 500 to 4,000 volts, which was in turn calibrated up to 1,000 volts by means of a battery of storage cells whose potential was determined in steps with an accurate Weston voltmeter.

To avoid any deterioration in the gas with use, a slow stream of air was kept continually flowing through the apparatus by means of a suction pump attached to the opening *V*. Before entering the apparatus at *U* the air was dried by passing through a tower of calcium chloride. A long tube filled with cotton was also interposed near *U* for the removal of dust.

TESTS OF APPARATUS.

4. As it is desirable that the apparatus should give results which approximate to what would be obtained with a very long point opposite an infinite plane, and should be as far as possible independent of the presence of the enclosure, some experiments were carried out to see how far these conditions were fulfilled.

In the first place it was found that the plate used was sufficiently large to satisfy the condition named. With a point at a distance of 1.5 cm. from the plate in the open air, the current obtained with a

given potential was the same as when a plate of twice its diameter was substituted.

The next experiment performed was to determine whether the length of the wire points used (1.5 cm.), attached as they were to the long rod N, was sufficient to give the same results as if they were infinitely long. Two points of the same diameter (.26 mm.) and 1.5 cm. and 5 cm. long respectively, were tried in succession in the apparatus at a distance of 1.5 cm. from the plate and the results obtained were again identical. It is not possible to use fine points longer than 1.5 cm. as they are set into vibration by the discharge.

The influence of the cylindrical vessel upon the results was determined by taking readings with a point (.19 mm. in diam.) at different distances from the plate, first with the plate in the open air and next with the plate inside the vessel, undried air being used.

The following results were obtained.

Distance of Point from Plane.	Voltage of Point.	Current in Vessel.	Current in Open Air.
1.0 cm.	6,000 volts.	65.0 divs.	64.5 divs.
1.5	7,500	70.5	68.0
2.0	8,500	71.5	68.2
2.5	9,000	59.5	62.0
3.14	9,500	47.5	54.5

The results indicate that contrary to what might be expected the effect of the vessel is to increase the current when the point is near to the plate, the increase being about 1 per cent. for a distance of 1 cm. and about 3.5 per cent. for a distance of 1.5 cm. At the larger distances the presence of the vessel diminished the current obtained by the plate.

We may account for the increase of current at short distances by con-idering the effect that the surrounding cylinder has of spreading the lines of force as they approach the plate. This enables a larger total current to flow and, roughly speaking, as long as the area to which the ions go does not extend beyond the limits of the plate the current received by it is increased.

Difficulties and Irregularities.

5. There is a disadvantage in having a short distance between the point and the plane in that it is more difficult to get a steady and

pure point discharge. This rarely caused trouble with the positive discharge, but with the negative discharge it was often impossible to get a steady discharge at all with certain points, especially those of a large diameter. Usually the current was more apt to become intermittent at its higher values, but the opposite was sometimes true that a current unsteady at first became uniform as it was increased.

To test the steadiness or intermittence of the current, the telephone receiver T was put into the galvanometer circuit. The intermittence is often due to the superposition of an intermittent effect upon the steady point discharge. Sometimes this constitutes such a small part of the whole current as not to affect the results appreciably. Clicks are heard in the telephone at intervals of a second or more, little specks of light appearing on the surface of the point as if little disruptive discharges were taking place. In such cases, as the current is increased the clicks increase in frequency until the current due to this cause becomes at least a considerable part of the whole. The pitch of the sound heard in the telephone increases with the current and becomes at times so high that it is a question whether sometimes the intermittence may not be so rapid that the telephone and the ear fail to detect it.

The luminous aspect of the discharge, too, serves to determine its nature, since when the light is not confined to the neighborhood of the point itself the discharge is no longer a pure point discharge.[1]

6. The potential at which the discharge from some points begins is different from that at which the current ceases, and the discharge shows other irregularities for small currents. This is especially true for the negative discharge. By exposing such points to certain radiations, Gorton and Warburg[2] found that the potentials at which the current begins and ends become the same. During all of the experiments to be described a glass tube (Z, Fig. 1) containing 1 gram of 1 per cent. radium bromide was placed at the side of the vessel R. The presence of this tube had no effect upon the larger currents from the points, but it served to make the discharge begin more regularly in the cases referred to above.

[1] J. Stark, Verh. der Deutsch. Phys. Gesell., VI., p. 115.

[2] Gorton and Warburg, Annal. der Physik, 18, p. 128, 1905.

The positive discharge was found on the whole very regular and steady for the large variety of points. As the voltage was increased the current started gradually from zero value (at least the initial current was less than 2×10^{-9} amp.), and at any one voltage underwent but slight variations. When a series of readings for the current was taken with increasing voltages and then repeated with decreasing voltages the values obtained were found to be practically identical, and the potential at which the current ceased was the same as that at which it began.

In the case of the negative discharge, however, the current was apt for certain points to begin with little jerks and to undergo some fluctuations, more especially at its lowest values. On reducing the voltage after the current had been running for some time, the values of the currents obtained were apt to be less than the corresponding ones found before. For most of the points, after they had been used, the current would stop and only begin again at a somewhat higher voltage than was necessary to start it in the first place.

Procedure in Experiments.

7. After a new point had been adjusted in the apparatus and the vessel closed, a stream of dry air was drawn through for some time before the taking of readings was begun. The minimum potential necessary to start a current was then determined first of all, and after this the values of the current were obtained for increasing voltages up to the limit of supply of the machine. Then a smaller number of readings was usually taken with decreasing voltages.

When the voltage for the initial current was determined the sensibility of the galvanometer was 10^{-8} amp. per division on the scale, while for most of the other readings the sensibility was reduced to one tenth of that value.

The potentials for which the currents from the points were determined were usually adjusted so as to have the reading of the voltmeter come exactly on one of its subdivision marks, as this permitted a more exact determination.

Inasmuch as the discharge from points is dependent upon the pressure and temperature of the air, it was necessary to find the magnitude of the variation due to these causes in order to be able

to reduce the different observations to a common condition. The manner in which these corrections were obtained is given in § 20 and § 21. The readings actually taken are given in the tables in each case, but in plotting the results they are all reduced to a pressure of 74 cm. of mercury and a temperature of 22° C., as these values are near to the mean conditions prevailing during the experiments.

POSITIVE DISCHARGE FROM POINTS WITH HEMISPHERICAL ENDS. DISTANCE = 1.5 CM.

8. The readings obtained for the positive discharge from cylindrical points of different diameters, with hemispherical ends (see *A*, Fig. 1) at a distance of 1.5 cm. from the plate, are given in Table I.

TABLE I.

Positive Discharge from Cylindrical Points with Hemispherical Ends. Distance from Plate = 1.5 cm.

Point Number.	1	2	3	4	5	6	7	8	9
Diameter in mm.	.0244	.039	.091	.174	.244	.50	.73	1.13	2.005
Pressure in cm.	73.0	74.9	74.1	74.1	74.1	74.1	74.1	73.7	73.2
Temperature in °C.	19	21.5	26.5	27.0	27.0	27.0	25.7	26.5	25.5
Starting potential.	1,600	2,000	2,450	3,015	3,365	4,600	5,500	6,700	9,150
Potentials in Volts, with Corresponding Currents in 10^{-7} Amperes.	1,750	3,000	2,500	3,255	3,500	5,000	5,800	7,000	9,250
	.28	7.2	.5	2.2	1.1	4.8	4.4	6.1	3.3
	2,000	4,000	3,000	3,500	4,000	6,000	6,000	8,000	9,500
	1.5	20.5	4.5	4.5	6.3	22.5	9.3	26.6	12.8
	2,500	5,000	4,000	4,000	5,000	7,000	7,000	9,000	9,750
	5.2	37.2	16.9	10.7	20.8	44.0	28.7	57.7	21.1
	3,000	6,000	5,000	5,000	6,000	8,000	8,000	10,000	10,000
	9.6	62.2	33.8	25.4	41.7	69.9	52.0	99.9	30.0
	4,000	7,000	6,000	6,000	7,000	9,000	9,000		10,500
	23.7	90.2	56.6	46.8	65.9	108.7	88.4		46.6
	5,000	8,000	7,000	7,000	8,000		10,000		
	42.9	124.3	85.1	73.2	95.2		131.2		
	6,000		8,000	8,000					
	68.9		117.2	102.0					
	7,000		8,500	8,700					
	100.6		139.7	131.8					
	8,000								
	135.6								

The table includes the results that were obtained under the conditions given with all of the points used. In cases where readings were repeated the average value is given.

All of the points except nos. 1 and 2 were made of brass wires, the ends being made round on a lathe for the larger points and by careful grinding on a stone for the smaller points. These last appeared quite round under the microscope, except no. 3 which was rather imperfect being too fine to work properly. Point no. 2 was made

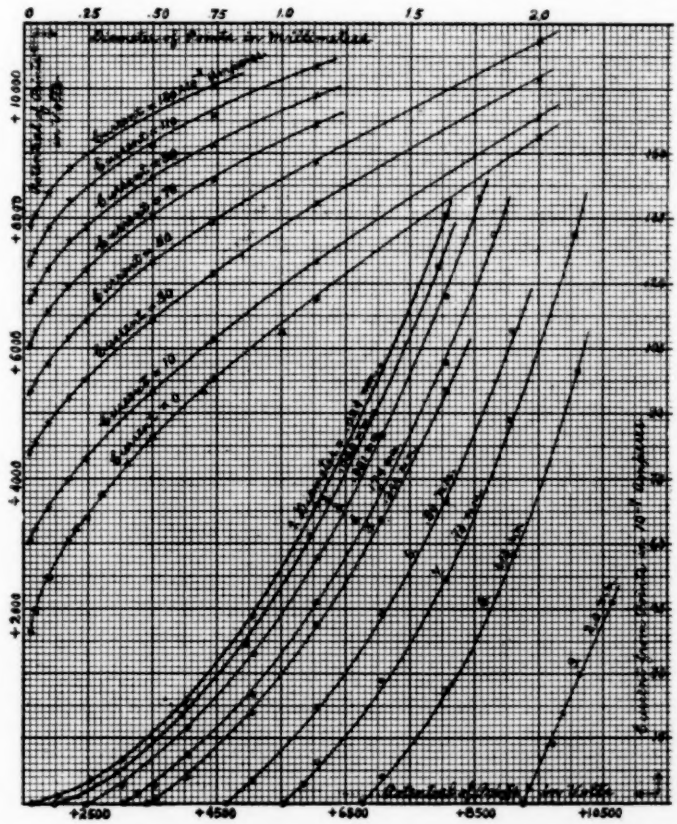

Fig. 2. Positive discharge in dry air from cylindrical points with hemispherical ends. Distance from plate = 1.5 cm. Pressure = 74 cm. Temperature = 22° C.

from a fine platinum wire, and point no. 1 was made from a silver covered platinum wire, the silver being completely dissolved from the end for a distance of 3 mm. The general appearance of the ends of these wires is shown by *C* and *D* respectively in Fig. 1.

9. The results, reduced to a pressure of 74 cm. and a temperature of 22° C. are shown graphically in the lower part of Fig. 2.

The regularity of the results is noted from the good agreement of the different points with their respective curves. It is not directly apparent, however, whether there is any regular relation between the results obtained for the different points and the diameters of these points. To show this, the system of curves in the upper part of the figure was drawn. Here each curve represents the relation between the size of the points and the voltage required to produce a current of the magnitude stated. The values for current = 0 are evidently the starting potentials. The regularity of the results is remarkable for observations of this character, and proves that no irregularities due to surface or other conditions enter into the experiments to a sufficient amount to overshadow the effect of the size of the points. Because of this regular relation it is now possible to use these curves for constructing the potential current curve for a point of any size by plotting the potentials corresponding, for the size in question, to the different currents given. Furthermore, by using such a curve it is quite possible to adopt a point and plane of the character here described, for measuring high potentials with a fair accuracy by simply noting the current flowing to the plate. Corrections for differences of pressure and temperature can be made in the manner given in §§ 20 and 21.

RELATION BETWEEN CURRENT, VOLTAGE, MINIMUM POTENTIAL, AND DIAMETER OF POINTS.

10. The results obtained with points differing so much in size give a severe test to any formula that may be proposed for the relation between the current and potential in point discharge. Several such formulæ have already been applied to different cases of point discharge.[1] Of these, Warburg's formula, $C = aV(V - M)$, best represents the above results for points of all sizes and currents of all values. In this formula, C is the current corresponding to a voltage V, M is the minimum potential required to start a current, and "a" is a constant depending upon the nature of the point and the

[1] E. Warburg, Wied. Annal., 67, p. 72, 1899. H. Sieveking, Annal. der Physik, 1, p. 303, 1900. F. Tamm, Annal. der Physik, 6, p. 259, 1901. P. Ewers, Annal. der Physik, 17, p. 781, 1905.

arrangement of the apparatus. It is apparent from the change in the slope of the curves in Fig. 2 that this constant "a" increases as the diameter of the point increases, and it was found that this increase is very nearly a linear one. For this reason it is possible to represent the whole system of curves by one formula involving the diameter of the points. The formula obtained from the above results for the discharge current in amperes under the conditions named is,

$$C = 2.58 \times 10^{-13}(1 + .110d)V(V - M),$$

d being the diameter of the point in millimeters.

In Table II. a comparison is made of some currents calculated by this formula, with the observed values taken from the potential current curves.

TABLE II.

Comparison of Observed Currents with those Calculated by the Formula
$C = 2.58 \times 10^{-13}(1 + .110d)\ V\ (V - M)$.

Diameter of Point.	.024	.039	.091	.174	.244	.50	.73	1.13	2.00
M.	1,620	1,980	2,470	3,050	3,400	4.650	5,530	6,770	9,250
V.	2,500	2,500	3,000	3,500	4,000	5,000	6,000	7,000	9,500
C. calc.	5.7	3.4	4.1	4.1	6.3	4.8	7.8	4.6	7.5
observ.	5.0	3.3	4.3	4.6	6.2	4.9	7.9	3.6	8.1
V.	3,000	3,000	3,500	4,000	4,500	5,500	6,500	7,500	10,000
C. calc.	10.8	7.9	9.4	10.0	13.1	12.7	17.6	15.8	23.6
observ.	9.9	7.7	9.5	10.1	12.5	12.7	16.8	13.0	25.3
V.	4,000	4,000	4,500	4,500	5,000	6,000	7,000	8,000	10,500
C. calc.	24.6	20.9	23.8	17.2	21.2	22.1	28.7	28.6	41.3
observ.	23.6	20.7	24.3	17.0	20.4	21.9	27.2	24.6	42.0
V.	5,000	5,000	5,500	5,500	6,000	7,000	8,000	8,500	
C. calc.	43.8	39.1	43.4	35.3	41.4	46.0	54.4	42.7	
observ.	42.8	38.9	43.9	34.7	40.3	42.1	52.7	38.3	
V.	6,000	6,000	6,500	6,500	7,000	8,000	9,000	9,000	
C. calc.	68.0	62.4	68.3	59.0	66.6	73.1	87.3	58.2	
observ.	68.0	62.7	68.7	57.0	64.4	68.7	85.7	54.3	
V.	7,000	7,000	7,500	7,500	8,000	9,000	10,000	10,000	
C. calc.	97.6	91.0	98.2	88.1	97.4	106.6	124.5	93.6	
observ.	99.6	93.4	98.7	84.7	93.7	105.0	129.3	94.3	
V.	8,000	8,000	8,500	8,500					
C. calc.	132.0	124.8	132.4	122.0					
observ.	134.0	127.2	135.9	119.3					

The agreement while not all that might be desired is nevertheless a fairly good one when everything is considered. It must be noted especially that since the current increases more rapidly than the voltage, the largest deviations between the observed and the calculated values of the current are due to but 2 per cent. change of voltage. Still, this difference is larger than the observational errors and either the relation given is only an approximate one or there was enough irregularity about the points or the discharge from them, to produce this difference.

11. The relation between the size of the point and the voltage for which the discharge begins (M in above formula) is a matter of

TABLE III.

Positive Discharge from Cylindrical Points with Hemispherical Ends. Distance from Plate = 1 cm.

Point Number.	1	2	3	4	5	6	7
Diameter in mm.	.039	.091	.174	.244	.50	1.13	2.00
Pressure in cm.	74.9	72.5	72.5	72.5	72.5	72.5	74.8
Temperature in °C.	20.5	24.2	24.2	24.2	24.2	24.2	26.0
Starting Potential.	1,895	2,300	2,850	3,200	4,425	6,350	8,750
Potentials in Volts, with Corresponding Currents in 10^{-7} Amperes.	2,000	2,500	3,000	3,500	4,500	6,500	9,000
	1.5	1.9	1.9	5.0	1.3	6.1	13.3
	3,000	3,000	4,000	4,000	5,000	7,000	9.250
	12.8	8.3	20.0	14.4	13.3*	22.2	28.9
	4,000	4,000	5,000	5,000	6,000	7,500	9,500
	33.3	28.9	46.6	38.9	44.4*	38.9	45.0
	5,000	5,000	6,000	6,000	7,000	8,000	9,750
	60.5	57.7	83.3	73.3*	83.8*	60.0	59.9
	6,000	6,000	7,000	7,000	8,000	8,500	10,000
	101.0	97.1	127.6	116.6*	132.1*	88.8	76.6
	7,000	7,000			8,300	9,000	10,250
	149.9	128.8			151.0*	119.9	93.3
						9.250	10,500
						138.8	106.0

For the values marked by a star, the current showed some intermittence.

considerable interest. No simple relation was found to hold well for the whole series of points.

Nevertheless up to a diameter of .7 mm., the values of M when

diminished by a constant number were found to be quite closely proportional to the square roots of the diameters of the points. This relation is given numerically for the above case by the formula, $M = 5{,}465\sqrt{d} + 755$, d being the diameter of the point in millimeters. This indicates that with an infinitely fine wire it would still require a potential of 755 volts to start the positive discharge to a plate 1.5 cm. distant. Some values obtained from the above formula have been plotted as triangles on the curve for $C = 0$ in Fig. 2, and it is seen that there is a good agreement with the observed values up to the limit stated.

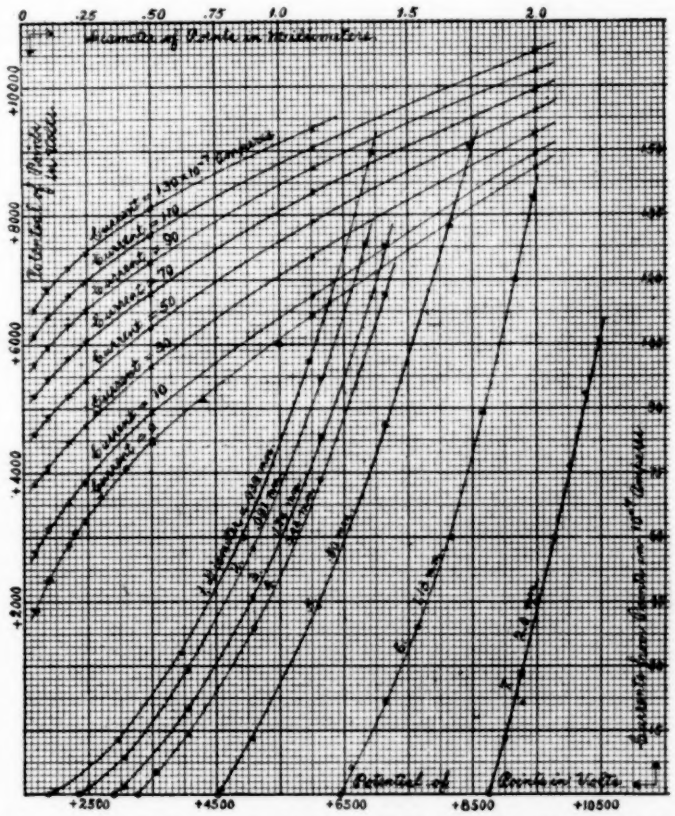

Fig. 3. Positive discharge in dry air from cylindrical points with hemispherical ends. Distance from plate = 1. cm. Pressure = 74 cm. Temperature = 22° C.

Above a diameter of .5 mm. the observed values for M are strictly proportional to the square roots of the diameters of the points and may be calculated by means of the formula, $M = 6{,}420\sqrt{d}$.

POSITIVE DISCHARGE FROM POINTS WITH HEMISPHERICAL ENDS. DISTANCE = 1 CM.

12. The results obtained for the positive discharge from cylindrical points having hemispherical ends when placed at a distance of 1 cm. from the plate, are given in Table III. The points used were the same as the ones of corresponding size in Table I.

TABLE IV.

Comparison of Observed Currents with those Calculated by the Formula $C = 4.05 \times 10^{-13} (1 + .235d) V(V - M)$.

Diameter of Point.	.039	.091	.174	.244	.50	1.13	2.00
M.	1,870	2,320	2,900	3,250	4,500	6,450	8,730
V.	2,500	3,000	3,500	3,500	5,000	7,000	9,000
C. calc.	6.4	8.4	8.8	3.8	11.3	16.5	14.5
observ.	6.3	8.3	9.4	3.8	11.6	17.3	14.3
V.	3,500	4,000	4,000	4,000	5,500	7,500	9,500
C. calc.	23.2	27.8	18.5	12.8	24.9	40.7	43.5
observ.	22.3	27.4	19.1	12.9	25.6	34.9	43.6
V.	4,000	4,500	4,500	4,500	6,000	8,000	10,000
C. calc.	34.7	40.6	30.3	24.0	40.8	64.0	75.5
observ.	33.7	40.0	30.8	23.7	41.0	54.6	75.0
V.	4,500	5,000	5,000	5,000	6,500	8,500	10,500
C. calc.	48.3	55.4	44.2	37.5	58.9	89.5	110.5
observ.	47.0	54.6	44.8	37.3	58.7	79.7	108.0
V.	5,000	5,500	5,500	5,500	7,000	9,000	
C. calc.	63.9	72.4	60.2	52.9	79.2	118.0	
observ.	63.3	71.5	60.2	52.3	79.3	108.2	
V.	5,500	6,000	6,000	6,000	7,500	9,500	
C. calc.	81.6	91.4	78.1	70.6	102.0	148.5	
observ.	81.7	91.3	78.3	69.9	101.4	142.5	
V.	6,000	6,500	6,500	6,500	8,000		
C. calc.	101.1	112.3	98.5	90.5	127.0		
observ.	103.5	113.0	98.9	89.9	125.5		
V.	6,500	7,000	7,000	7,000	8,500		
C. calc.	122.8	135.5	120.8	112.5	154.1		
observ.	127 0	136.6	120.7	111.5	153.0		

The results, reduced to a pressure of 74 cm. and a temperature of 22° C., are shown graphically in the lower right hand part of Fig. 3.

The curves in the upper left hand part of the figure again show

the relation between the diameter of the points and the potential required to produce the current given in each case. The same regularity appears in the results as in those above and these curves may here too be used for constructing the potential current curve for a point of any size, when placed at a distance of 1 cm. from the plate.

13. The results shown by the family of potential current curves in Fig. 3 may all be well represented by the formula,

$$C = 4.05 \times 10^{-13}(1 + .235d)V(V - M),$$

as is seen from Table IV. where a comparison is made of the observed and calculated values of the current for various potentials. The

TABLE V.

Positive Discharge from Cylindrical Points with Plane Ends. Distance from Plate = 1.5 *cm.*

Point Number.	1	2	3	4	5	6	7	8	9
Diameter in mm.	.088	.197	.267	.466	.516	.808	1.17	1.68	2.18
Pressure in cm.	73.7	73.7	73.7	73.0	74.8	73.9	73.9	74.1	74.1
Temperature in °C.	26.5	26.5	25.5	20.7	27.5	23.0	23.0	27.5	27.5
Starting potential.	2,440	3,175	3,550	4,475	4,750	5,750	6,800	8,015	9,050
Potentials in Volts, with Corresponding Currents in 10^{-7} Amperes.	2,500	3,500	4,000	5,000	5,000	6,000	7,000	8,250	9,250
	.8	2.8	4.4	7.3	4.4	5.0	4.4	8.4	10.7
	3,000	4,000	5,000	6,000	6,000	7,000	8,000	8,500	9,500
	4.4	9.4	19.4	27.0	23.3	26.6	28.9	17.5	21.4
	4,000	5,000	6,000	7,000	7,000	8,000	9,000	9,000	9,750
	17.2	25.0	41.1	50.7	47.2	53.3	65.5	37.7*	31.6
	5,000	6,000	7,000	8,000	8,000	9,000	10,000	9,500	10,000
	34.4	47.7	66.0	79.4	76.6	92.1	113.2	61.4*	42.8
	6,000	7,000	8,000	9,000	9,000	9,750		10,000	10,500
	59.9	74.4	96.6	119.4	117.7	129.3		83.4*	63.2
	7,000	7,725	9,000						
	86.0	95.5	139.9						
	8,000								
	122.2								

calculated values for the point whose diameter is 1.13 mm. are all somewhat high and M would have to be increased by 100 volts to bring the numbers into good agreement with the observed results.

The relation between the minimum potential and the diameter of the points is similar to that found for the points at a distance of 1.5 cm. from the plate. Up to a diameter of .7 mm. the values of M may be quite accurately calculated by the equation, $M = 5{,}340\sqrt{d} + 675$. Some values obtained by the use of this formula are plotted as triangles on the curve for $C = 0$, in Fig. 3, and it is seen that they

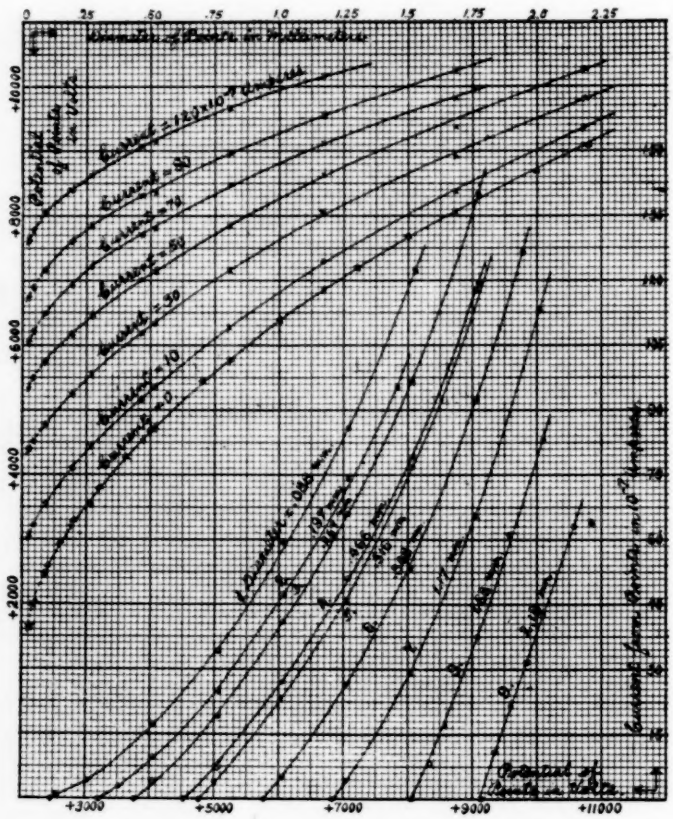

Fig. 4. Positive discharge in dry air from cylindrical points with plane ends. Distance from plate = 1.5 cm. Pressure = 74 cm. Temperature = 22° C.

agree well with the observed values. For diameters larger than .7 mm. the calculated values come out too small and another formula of the same type is necessary to represent the results.

POSITIVE DISCHARGE FROM POINTS WITH PLANE ENDS. DISTANCE FROM PLATE = 1.5 CM.

14. The results obtained for the positive discharge from cylindrical points with plane ends (see *B*, Fig. 1) are given in Table V. The distance of the points from the plate was 1.5 cm. The points were all made from brass wires.

15. The results, reduced to a pressure of 74 cm. and a temperature of 22° C., are shown graphically in the lower part of Fig. 4.

The relation between the diameter of the points and the potential required to produce any given current is shown for a number of currents by the series of curves in the upper left hand portion of

TABLE VI.

Comparison of Observed Currents with those Calculated by the Formula $C = 2.60 \times 10^{-13} (1 + .30d)\ V(V - M)$.

Diameter of Point.	.088	.197	.267	.466	.516	.808	1.17	1.68	2.18
M.	2,460	3,200	3,760	4,510	4,720	5,770	6,830	8,080	9,100
V.	3,000	3,500	4,000	5,000	5,000	6,000	7,000	8,500	9,500
C. calc.	4.3	2.9	2.7	7.3	4.2	4.6	4.0	14.0	16.4
observ.	4.2	2.7	3.3	7.4	4.3	4.3	4.0	14.0	17.5
V.	4,000	4,500	5,000	6,000	6,000	6,500	7,500	9,000	10,000
C. calc.	16.4	16.1	17.4	26.5	23.1	15.8	17.1	32.6	39.7
observ.	16.2	16.0	19.1	26.2	22.8	14.3	15.3	33.8	39.1
V.	5,000	5,000	6,000	6,500	6,500	7,000	8,000	9,500	10,500
C. calc.	33.9	24.7	37.7	38.4	34.8	27.8	31.7	52.6	63.4
observ.	33.9	24.5	39.4	37.1	33.7	26.0	28.8	56.0	60.6
V.	6,000	5,500	7,000	7,000	7,000	7,500	8,500	10,000	
C. calc.	56.7	34.8	63.5	51.6	47.9	42.0	48.2	74.9	
observ.	56.7	34.6	64.4	50.0	46.7	38.8	45.3	79.8	
V.	6,500	6,000	7,500	7,500	7,500	8,000	9,000		
C. calc.	70.1	46.2	78.8	66.3	62.5	57.7	66.2		
observ.	70.0	45.7	78.8	63.7	60.5	53.0	65.4		
V.	7,000	6,500	8,000	8,000	8.000	8,500	9,500		
C. calc.	85.0	59.0	95.1	82.4	78.7	75.1	86.1		
observ.	85.0	58.0	95.4	80.0	76.6	70.6	87.6		
V.	7,500	7,000	8,500	8,500	8,500	9,000	10,000		
C. calc.	100.9	73.1	113.1	100.7	96.5	94.0	107.6		
observ.	101.2	71.5	114.7	97.9	95.1	91.6	110.9		
V.	8,000	7,500	9,000	9,000	9,000	9,500			
C. calc.	118.8	88.6	132.2	119.6	115.6	114.6			
observ.	118.7	86.5	136.2	116.7	115.0	113.3			

the figure. As it is seen that the results for the smallest points are almost identical with those obtained with points having hemispherical ends, as shown in Fig. 2, the values obtained in the latter case for the two fine platinum wires (nos. 1 and 2) are added here and the curves extended through them as broken lines. For the larger points the potential required to produce a given current is smaller for points with plane ends than it is for points with hemispherical ends.

16. The relation between the current and the potential and the size of the points can be represented in this case by the formula,

$$C = 2.60 \times 10^{-13}(1 + .30d)V(V - M),$$

and some values of the current calculated by this formula for various potentials are compared in Table VI. with the observed values taken from the curves in Fig. 4.

The relation between the minimum potential M and the diameter of the points d can in this case be represented throughout the whole range of diameters used by the formula, $M = 5{,}670\sqrt{d} + 705$. Some values obtained from this formula are plotted as triangles on the curve for $C = 0$ in Fig. 4, and it is seen that they are in good agreement with the observed values.

NEGATIVE DISCHARGE.

17. The results obtained for the negative discharge from cylindrical points with hemispherical ends, at a distance of 1.5 cm. from the plate, are given in Table VII. The points used were the same as those of corresponding size employed for the positive discharge. The currents from the larger points were all intermittent and so are not given. In a few of the readings given the current was partly or wholly intermittent and such values are marked by a star. The smaller currents from point no. 4 were of this character and it is noticed that their value is less than what an agreement with the other results would require.

The above results, reduced to a pressure of 74 cm. and a temperature of 22° C., are represented by the curves shown in the lower part of Fig. 5.

The relation between the diameter of the points and the voltage

TABLE VII.

Negative Discharge from Cylindrical Points with Hemispherical Ends.
Distance from Plate = 1.5 cm.

Point Number.	1	2	3	4	5	6
Diameter in mm.	.0244	.039	.091	.174	.244	.50
Pressure in cm.	73.0	74.9	74.1	74.1	74.1	74.1
Temperature in °C.	19.0	21.5	26.5	27.0	27.0	27.0
Starting Potential.	1,125	1,475	1,975	2,775	3,100	4,650
Potentials in Volts, with Corresponding Currents in 10^{-7} Amperes.	1,250	2,000	2,000	3,000	3,500	5,000
	.3	4.1	.3	.6	7.2	10.6
	1,500	3,000	2,500	3,500	4,000	6,000
	1.8	16.5	5.0	1.5*	15.5	32.2*
	2,000	4,000	3,000	4,000	5,000	7,000
	5.4	39.1	12.5	13.9*	43.0	77.7
	3,000	5,000	4,000	5,000	6,000	7,500
	20.2	69.3	33.9	52.2	81.6	99.9*
	4,000	6,000	5,000	6,000	6,500	
	44.8	112.8	63.8	95.9	113.2	
	5,000	6,500	6,000	6,250		
	77.3	135.9	104.3	105.5		
	6,000		6,500			
	122.6		119.9			
	6,350					
	138.9					

required to produce a given current is again shown by the curves in the upper part of the figure. It is to be noticed that the voltage required to produce a given current here increases more rapidly with the diameter of the points than it did in the case of the positive discharge.

The results obtained throughout with the negative discharge do not permit of having the relation between the current, voltage and the diameter of the points, consistently represented by a formula as simple as served for the positive discharge. The discharge tending more to intermittence and irregularity seems to depend more on the surface conditions of the point than in the case of the positive discharge, and it may be too that some of the irregularity is due to the composite character of the gas, the current changing somewhat, especially at its lowest values, between the various components.

The relation between the diameter of the points d and the minimum potential M is represented by the formula $M=6{,}400\sqrt{d}+90$. Some values of M obtained from this formula are marked as triangles on the curve for $C = 0$ in Fig. 5.

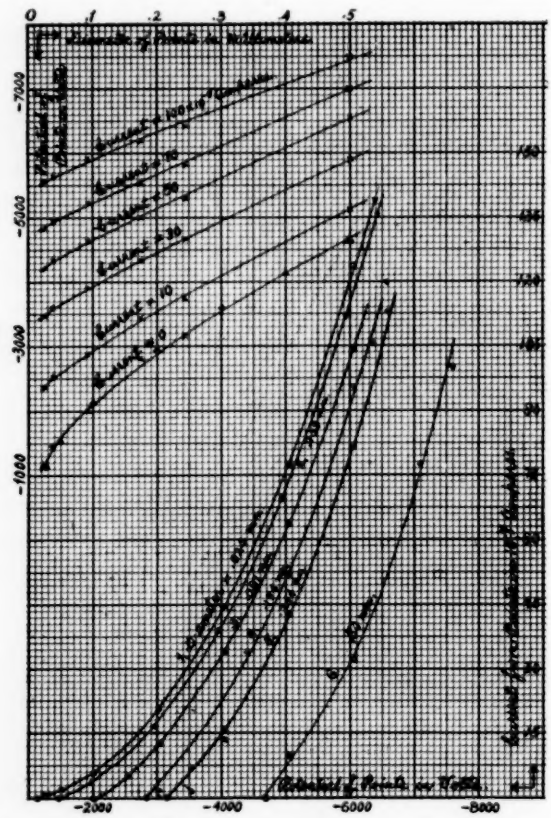

Fig. 5. Negative discharge in dry air from cylindrical points with hemispherical ends. Distance from plate = 1.5 cm. Pressure = 74 cm. Temperature = 22° C.

18. It was still more difficult to get a steady negative discharge while using the same points as above at a distance of 1 cm. from the plate. The few steady results that were obtained are given in Table VIII., and the corresponding values reduced to a pressure of 74 cm. and a temperature of 22° C. are shown graphically in Fig. 6. They appear rather irregular, possibly because of one of the last two points. The relation between the minimum potential and

the diameter of the points, as roughly given by the curve for $C = 0$ in the upper part of the figure, is represented by the formula $M = 5{,}300\sqrt{d} + 385$. The triangles on the curve named represent values obtained by the use of this formula.

TABLE VIII.

Negative Discharge from Cylindrical Points with Hemispherical Ends. Distance from Plate = 1 cm.

Point Number.	1	2	3	4
Diameter in mm.	.039	.091	.174	.267
Pressure in cm.	74.9	72.5	72.5	74.4
Temperature in ° C.	20.5	24.2	24.2	21.5
Starting Potential.	1,465	1,850	2.750	3,025
Potentials in Volts, with Corresponding Currents in 10^{-7} Amperes.	2,000	2 000	3.000	4,000
	7.7	1.1	3.0	35.2
	3,000	2,500	3,500	5,000
	30.3	9.9	23.1	89.7
	4,000	3,000	4,000	5,500
	71.5	23.7	46.2	133.1
	5,000	4,000	5,000	6,000
	130.9	64.9	104.5	171.6
	5,500	5,000	5,500	
	170.5	126.5	150.7	

19. The results obtained for the negative discharge from cylindrical points with hemispherical ends at a distance of 1.5 cm. from the plate, are given in Table IX. They are represented graphically by the curves in the lower part of Fig. 7, and the relation between the diameter of the points and the potential required to produce a given current, is shown by the curves in the upper part of the figure. The results for the two fine platinum wires, nos. 1 and 2 of Table VII., are included here also because of the agreement of the two sets of results for the smaller points, the curves being extended through them as broken lines.

The relation between the minimum potential M, and the diameter of the points d, is given in this case by the formula, $M = 5{,}545\sqrt{d} + 335$. The points shown by triangles on the curve for $C = 0$ in Fig. 7 represent values calculated by the use of this formula.

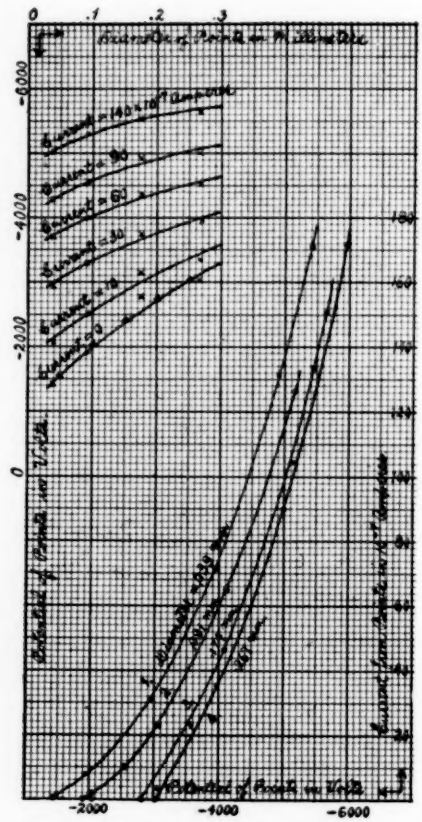

Fig. 6. Negative discharge in dry air from cylindrical points with hemispherical ends. Distance from plate = 1 cm. Pressure = 74 cm. Temperature = 22° C.

VARIATION OF DISCHARGE WITH PRESSURE.

20. Since the discharge is dependent upon the pressure of the air which varied from day to day, it was necessary to determine the magnitude of this effect so as to be able to reduce the results to a common pressure.

For doing this the apparatus was sealed so as to permit of its being partially exhausted. Sets of readings for both the positive and negative discharge were taken with a point .18 mm. in diameter at a distance of 1.5 cm. from the plate, with the air pressures at 51.8 cm., 63.4 cm., and 73.6 cm., the temperature being 19° C. The results obtained for the positive discharge are shown by the curves in Fig. 8.

TABLE IX.

Negative Discharge from Cylindrical Points with Plane Ends. Distance from Plate = 1.5 cm.

Point Number.	1	2	3	4	5	6
Diameter in mm.	.088	.19	.267	.51	.808	1.17
Pressure in cm.	73.7	73.7	73.7	74.8	73.9	73.9
Temperature in °C.	26.5	26.5	26.5	27.5	23.0	23.0
Starting potential.	1,850	2,750	3,100	4,350	5,300	6,350
Potentials in Volts, with Corresponding Currents in 10^{-7} Amperes.	2,000	3,000	3,500	4,500	5,500	6,500
	.7	4.2	8.3	5.5	7.7*	7.7
	3,000	4,000	4,000	5,000	6,000	7,000
	14.1	23.7	17.9	18.2	22.6	30.8*
	4,000	5,000	5,000	6,000	7,000	8,000
	36.9	51.7	44.0	55.0	62.7*	77.0*
	5,000	6,000	6,000	7,000	8,000	8,500
	67.6	92.4	83.1	101.2	110.0	102.8
	5,500	6,625	7,000	7,350		
	90.2	122.1	127.6	121.0		

The relation between the pressure and the potential required to maintain a given current is shown for a number of currents, by the curves in the upper part of the figure. It is seen that for this range the potential increases linearly with the pressure. The variation of voltage with pressure is expressed for each current under its curve, as a fraction of the voltage required to produce that current at a pressure of 74 cm. This fraction only increases from .0087 for a current of zero to .0100 for a current of 100×10^{-7} amperes, and the increase was assumed to be a linear one. By means of this relation the voltage for each current obtained in all of the experiments was readily reduced to that necessary to produce the same current at a pressure of 74 cm., the fraction given above being the part of itself that any voltage has to be diminished for each centimeter that the pressure was above 74 cm.

The results obtained for the negative discharge at the different pressures are shown in Fig. 9. From the curves in the upper part of the figure it is seen that the variation of the voltage with the pressure changes for the different currents from .0096 to .013 part of the voltage required to produce the given currents at 74 cm.

pressure. The increase in this fraction was assumed to be a linear one and the correction for pressure was applied to each of the results for the negative discharge in the same way as is explained above for the positive discharge.

VARIATION OF DISCHARGE WITH TEMPERATURE.

21. To get the magnitude of the corrections that must be applied to reduce the results to a common temperature, potential current

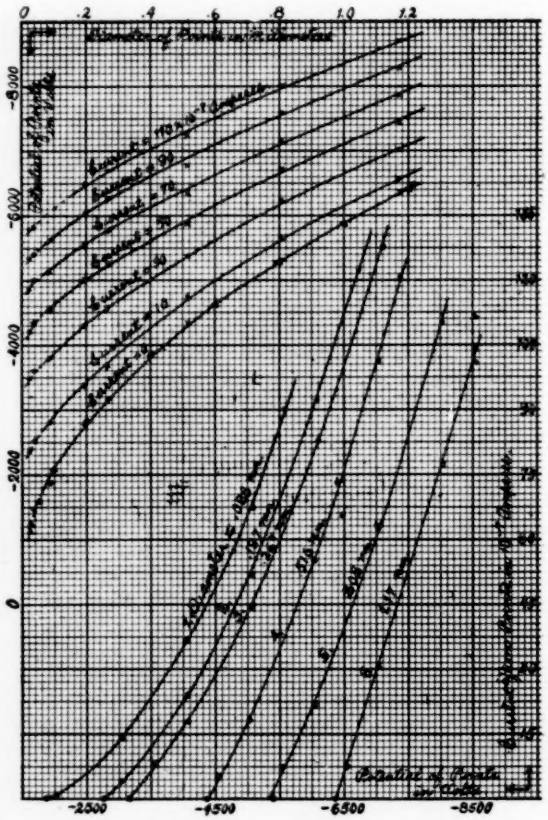

Fig. 7. Negative discharge in dry air from cylindrical points with plane ends. Distance from plate = 1.5 cm. Pressure = 74 cm. Temperature = 22° C.

curves were obtained for both the positive and the negative discharges with the apparatus at two different temperatures, using a point .091 mm. in diameter at a distance of 1.5 cm. from the plate.

The temperatures used were about 23° C. and about 0° C., the first being the ordinary temperature of the room, and the second being obtained by opening the laboratory windows and letting the whole

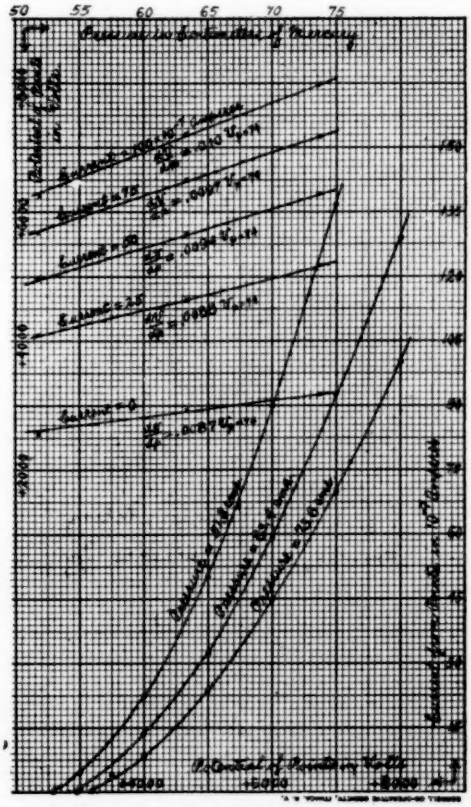

Fig. 8. Positive discharge in dry air at different pressures. Cylindrical point with spherical end. Diameter = .18 mm. Distance from plate = 1.5 cm. Temperature = 19° C.

room cool to that temperature. Three sets of readings were taken and the results of one of these are shown by the curves in Fig. 10. It is seen that at a lower temperature a larger voltage is required to produce the same current. A peculiarity appears in this set of readings for the positive discharge, since the curves for the two temperatures approach coincidence at the starting point. This did not repeat itself in the other two sets of readings taken, and the average effect calculated from all of the results was thought sufficiently accu-

rate for the purpose in hand. It was thus found that for every 1° C. decrease in the temperature, the voltage required to maintain any current increases by approximately .0018 part of itself for the positive discharge and by .0028 part of itself for the negative discharge. The effect may be due for the most part to a change in the air density, but the values are not sufficiently accurate to decide this. The number obtained for the negative discharge is in agreement with this supposition.

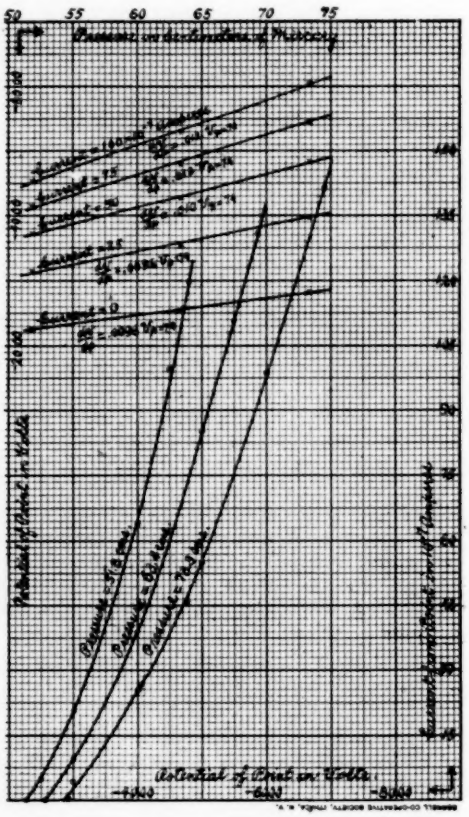

Fig. 9. Negative discharge in dry air at different pressures. Cylindrical point with spherical end. Diameter = .18 mm. Distance from plate = 1.5 cm. Temperature = 19° C.

The temperature and pressure corrections found in each case by the use of a point of one size only were assumed to hold alike for points of all sizes. The observations were, however, reduced to a pressure

and a temperature near to the mean of the conditions prevailing, so that the total correction applied was quite small in most cases and in only a very few was as high as two per cent.

General Remarks.

22. The ends of the wires used in the experiments were by no means free from minor irregularities in shape, but from the regularity of the results obtained with them it would appear that the

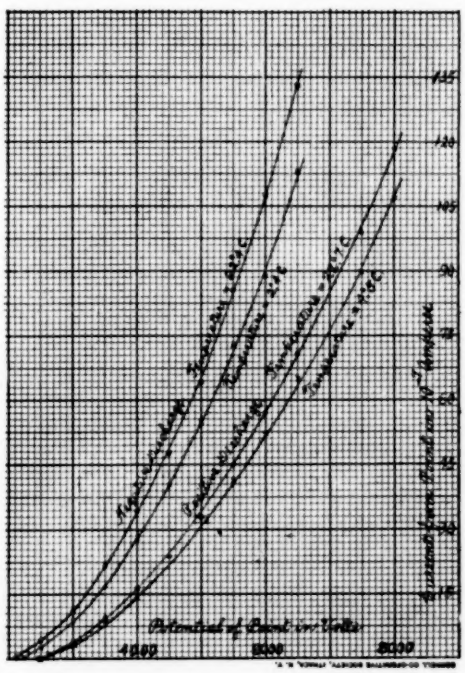

Fig. 10. Effect of temperature upon the discharge from a cylindrical point with a rounded end. Diameter = .091 mm. Distance from plate = 1.5 cm. Pressure = 74.85 cm.

discharge is fairly independent of such irregularities as are small compared to the size of the point, and depends only upon the general size and form of the point. Indeed the results obtained with the smallest points indicate that with them the ends may have large irregularities without affecting the results greatly.

The number that must be subtracted from the minimum potentials to make the results, up to a certain limit, proportional to the square

roots of the diameters of the points, were found for the best agreement in the three cases of the positive discharge, to be 755, 675 and 705. If the formulæ hold for minute values of the diameters, the above numbers indicate the voltage necessary to start a discharge for $d = 0$. The corresponding numbers obtained for the negative discharge, though far from being alike, average less than a half of the above numbers for the positive discharge. The ratio of the potentials necessary to start the two discharges with infinitesimal points would thus appear to be even larger than with points of a finite size, and this is in agreement with what is noticed, *i. e.*, that as the points get larger the two kinds of discharge start at more nearly the same potential relatively.

SUMMARY.

23. It has been shown how it is possible to select conditions for the discharge from pointed conductors so that the numerical results obtained may readily be reproduced with new points and apparatus. This is made possible for the most part by using points of such a simple and definite shape that they may easily be duplicated with sufficient accuracy. For this purpose it has been found that points made of cylindrical wires of a sufficient length, with their ends either rounded or plane are very convenient and give regular results depending only upon the diameters of the wires.

Curves are given from which it is possible to find the current that will flow in dry air, under the normal conditions given from a point of any size up to 2 mm. in diameter, for any given potential. Corrections are given also by means of which it is possible to extend the results to any temperature usually found in the room and to a considerable range of pressures near that of the atmosphere.

Voltages may be determined with fair accuracy by measuring the current flowing from a point of known size and using a potential current curve drawn for the particular point by the aid of the results here given.

The potential required to start a discharge and the diameter of the point are related, at least for a limited range, so that the minimum potentials minus a constant are proportional to the square roots of the diameters of the points. This relation holds especially well for points with plane ends.

The relation between the current from a point and its potential may be represented quite well for the positive discharge from any point by Warburg's formula, $C = aV(V - M)$. This formula is extended to include at once points of all sizes, by changing the constant "a" to $a(1 + bd)$, where d is the diameter of the point and a and b are new constants.

By embodying the relation between the minimum potential and the size of the point into this formula, it becomes possible by its means to calculate the current which will flow in dry air from a cylindrical point of any diameter when this is at any given potential and placed at a definite distance from a plate.

In a paper to follow the results will be given which have been obtained for the discharge from conical points of a definite angle and from steel needle points, as well as some other results on the discharge from points.

THE PHYSICAL LABORATORY,
UNIVERSITY OF MINNESOTA,
June 1, 1907.

POTENTIOMETER INSTALLATION.

ESPECIALLY FOR HIGH TEMPERATURE AND THERMOELECTRIC WORK.

BY WALTER P. WHITE.

THE increasing interest shown in high temperature research by scientific workers in different fields has suggested the publication of various methods which have recommended themselves in this laboratory.[1] The present paper deals with the thermoelectric measurement of high temperatures, and more particularly with the apparatus auxiliary to the thermoelement, which consists for the most part of commercial potentiometers of familiar type, with the usual accessories. In the installation of this apparatus, several simple modifications have greatly increased the efficiency, not only for the more specialized work of the laboratory, but for general work as well. The present paper, therefore, may prove of interest to some not especially concerned with high temperature research.

The work for which this apparatus is specially arranged is the determination of melting points and similar thermal phenomena in silicates and other refractory substances. The determinations are carried out by the familiar method of Frankenheim. A charge of the substance under investigation is heated in an electric furnace, whose temperature is continually measured and controlled; the variations in the temperature difference between charge and furnace indicate the changes going on in the charge. This method will soon form the subject of another article, and need not be further

[1] Brief descriptions of some of the apparatus and methods have already been given in connection with the published work of the laboratory as follows: Of the furnace and thermoelements, Day and Allen, Carnegie Institution Publication No. 31, PHYS. REV., 19, 17, 1904; of the general methods of measurement, Carnegie Institution Publication No. 31 (partly reprinted in Zeit. f. Phys. Chem., 54, 1, 1905); also Allen, White and Wright, Amer. Journ. Sci., 21, 89, 1906; Day and Shepherd, Amer. Journ. Sci., 22, 265, 1906; Allen, Wright and Clement, Amer. Journ. Sci., 22, 385, 1906; of the treatment of thermoelements, W. P. White, PHYS. REV., 23, 449, 1906 (Phys. Zeitschr., 8, 325, 1907).

considered here. The problem which it sets in electrical measurement may be stated as follows:

(*a*) Temperatures up to 1600° must be read to .1°; with a platinum-platin-rhodium thermoelement, .1° corresponds to about one millionth of a volt.

(*b*) The materials of the furnaces, and also the air, become ionized and conduct electricity at the temperatures generally employed. The potential difference in the heating coils is about 100 volts, that is, one hundred million times the allowable error of the measurements, yet leakage from the coils must not be allowed to affect the measuring system.

(*c*) The measurements consist in following two or more continually changing temperatures. The only effective way to accomplish this is to read the various temperatures in rotation at definite intervals. Two or more readings per minute are usually needed. The experimenter must also have time to note carefully the progress of his experiment, to regulate the temperature of the furnace, and so forth, and must still be freed as far as possible from hurry or fatigue, since mistakes can seldom be corrected during the progress of the heating. Manipulation must therefore be simplified and the apparatus must respond as quickly as possible. Quickness and simplicity, then, without sacrifice of sensitiveness or accuracy under trying conditions, are the qualities required of the electric measuring apparatus in silicate work. Even if less imperatively needed, they are obviously desirable in other work as well.

Melting point determinations at high temperatures have hitherto been mainly made either with the platinum resistance thermometer or with the direct reading thermoelectric pyrometer. Neither of these instruments meets the demands of silicate work.

The direct reading pyrometer lacks sensitiveness, since intervals smaller than 5° cannot be read with certainty.[1] The resistance thermometer is well known to be poorly adapted for temperatures

[1] This is the unavoidable error of a carefully calibrated instrument in first-class condition. Ordinarily, very much larger errors are present. For instance, the scales in different instruments from the same maker sometimes differ 6° at 1000, and thermoelements of the best make may vary 12°. Calibration errors of 10° at 1000 have also been observed in new instruments, while a surprising amount of care is needed to avoid much greater errors from faulty contacts.

above 1000°, and is therefore out of the question for nearly all silicates. (The stretching of the wires when hot, failure of the insulation and the disintegration of the platinum at higher temperatures, all affect the readings of the resistance pyrometer much more than those of the thermoelement.) Another disadvantage of the resistance thermometer in melting point work at all temperatures seems less generally appreciated. This is the relative bulk of the working portion, which must be completely covered by the substance examined, and which therefore necessitates using large quantities of material. Some of our best melting point determinations at high temperatures are now obtained with about 1 cu. cm. of substance, in which the bare thermoelement is directly inserted. For work of this character, the resistance thermometer is obviously out of the question.

The thermoelement read with a potentiometer meets all requirements of the present work. Readings can be made with practically the same ease as on a direct reading instrument, so that whatever difficulty there is in this direction is chargeable to the nature of the measurements, not to the apparatus. When properly installed, the potentiometer will remain for months ready for instant use, with no other attention than an occasional oiling of the switches. The accuracy is, of course, that of the themoelement, and has been sufficient for all work thus far undertaken. The elements are exposed to high temperatures for the shortest possible period and are used either in glazed porcelain tubes or in furnaces free from commercial platinum. Under such conditions, deterioration, though not entirely prevented, is slow.[1] By measuring to a millimeter the depth of insertion in the furnace, and by comparing occasionally with carefully kept standards, the relative error of the temperature measurements can be reduced to $\frac{1}{3}°$, which is a little less than other errors inherent in the work.

Partial Direct Reading. — Simplicity of manipulation and quickness are promoted by making the maximum use of a direct reading instrument, the galvanometer. Since a galvanometer alone, in the form of a voltmeter, is sufficient for rough measurements with

[1] In twenty determinations near 1350°, occupying about 10 hours, an element inserted 17 cm. in the furnace fell a little over 1°.

thermoelements, a moderate increase in its efficiency is all that is needed for the most refined work. Yet when a potentiometer is added to secure greater efficiency, the whole burden is often thrown upon the potentiometer, and the galvanometer is used merely to indicate when a balance is obtained. This practice has some obvious advantages, but is not justified where rapidity is important. If the galvanometer is provided with a scale reading directly in micro-volts, and is used through a rather wide range, the potentiometer adjustments may be confined to the larger units and greatly reduced in number. The quickness and simplicity of exclusively direct reading are thus approached with no sacrifice of accuracy.

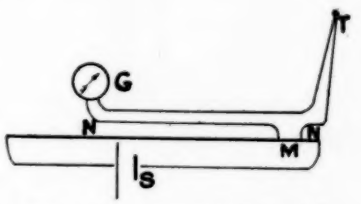

Fig. 1. To accompany formula 1.

A necessary requirement for this system is, of course, constant galvanometer sensibility, which is not found in ordinary potentiometer installations. I have elsewhere[1] shown how potentiometers can easily be constructed so as to give constant galvanometer sensibility. For ordinary instruments, and for the range needed in thermoelectric work, a sufficient approach to it can be obtained by inserting an extra variable resistance in the galvanometer circuit, as shown at R_A in Fig. 4. The operation of this resistance is as follows: Let Fig. 1 represent a simple potentiometer installation, where G indicates the resistance of the galvanometer, and T that of the thermoelement, whose electromotive force is balanced against the fall of potential along the resistance, M, in the main circuit. S is the storage cell of the main circuit, $M + N$ the total resistance in that circuit. The electromotive force of the thermoelement may be considered as equal to the sum of two others; one is equal and opposite to that given by the potentiometer setting, and has the effect of neutralizing the potentiometer electromotive force completely as far as any current through the galvanometer is concerned; the other, Δe, is the unbalanced electromotive force which is to be measured by the galvanometer, and which, by the well known principle that each electromotive force in a circuit produces its own

[1] Zeitschr. f. Instrumentenkunde, 27, 210, 1907.

current regardless of all others present, gives a current equal to

$$\frac{Je}{T + G + \frac{MN}{M + N}} \qquad (1)$$

Constant galvanometer sensibility is therefore secured by keeping the resistance $T + G + MN/M + N$ constant.

In measuring the comparatively small electromotive forces of platinum thermoelements, the resistance $MN/M + N$ differs but little from M; hence sufficient compensation is obtained if resistance is subtracted from the ballast, R_A, equal to that added to M in setting the potentiometer. An ordinary switch rheostat of very moderate accuracy is sufficient. The labor of making the adjustments is usually slight. For instance, if the resistance of the galvanometer circuit is 500 ohms and an accuracy of 0.5 per cent. is desired in reading the galvanometer, the resistance must not vary more than 2.5 ohms. The auxiliary must therefore be changed whenever the potentiometer resistance, M, has altered 5 ohms. In a potentiometer of 20,000 ohms total resistance, 5 ohms correspond to 500 microvolts, or from 40 to 50° with a platinum-platinum-rhodium thermoelement, and the adjustment will not need attention oftener than once in 15 minutes in ordinary work. In a potentiometer of 2,000 ohms total resistance, on the other hand, 5 ohms will correspond to from 400 to 500°; the adjustment can be made before the observations begin, and will then need no further attention. A potentiometer resistance moderately — but only moderately — low compared to that of the rest of the circuit may therefore be of advantage where constant galvanometer sensibility is desired. (A rather high resistance of the whole circuit is also desirable to reduce the effect of accidental variations in resistance due to the changing temperature of the thermoelement, to defective contacts, etc.) In classes of work where widely differing electromotive forces are to be measured in succession, the difficulty of maintaining constant galvanometer sensibility obviously increases, and the need is greater for a potentiometer of low resistance, or, better still, of constant branch circuit resistance.[1]

[1] H. B. Brooks has also, in his "deflection potentiometer" (Bull. Bureau of Standards, vol. 2, p. 225, 1906), made a systematic attempt to gain speed by increasing

The usefulness of the above method of relying largely upon the galvanometer will of course vary greatly under different circumstances. In melting point determinations, constant galvanometer sensibility is not only very easy to obtain, but is especially important, for the following reasons: (1) In the rapid reading of varying electromotive forces at definite time intervals, an exact balance of the potentiometer is out of the question. The galvanometer follows the varying electromotive force[1] and needs about as much time to reach its moving equilibrium as it requires to come to rest. Hence the nearest attainable approach to a balance is a potentiometer setting made a number of seconds before the time of reading. When that time arrives, the galvanometer nearly always shows a deflection which must be added to or subtracted from the potentiometer reading. Some use of the galvanometer as a deflection instrument is therefore unavoidable. The quantities read can, if desired, be kept within 20 microvolts, for which a sensibility constant to 5 per cent. is ample. (2) When once deflections of this magnitude have been provided for, however, an increase of the range to 100 or 200 microvolts causes very little further trouble. Moreover, in melting point determinations, such increase is especially advantageous. This is due to the fact that the temperature intervals concerned — those between the different elements as well as between successive readings of the same element — are usually more than ten and seldom over 200 microvolts. With the narrower galvanometer range, a separate setting of the potentiometer must be made twice each minute, involving a preliminary estimate, the setting of two or three switches, and afterward the addition of the readings obtained from both instruments. With the more carefully adjusted galvanometer, the potentiometer requires only to be advanced one unit every few minutes and the deflections are read and recorded directly from the scale. The saving in numerical work of various kinds is even more important than in switch manipulation, though

the use of the galvanometer. The small sensitiveness of this apparatus, and some of the other difficulties which Mr. Brooks ingeniously avoids, are due to the use of an insensitive pivot galvanometer, and, as his own discussion implies (p. 238) are not inherent in the method.

[1] Lagging behind it by a time interval which is approximately equal to T/π, if the galvanometer, of period T, is critically damped.

this latter may often be diminished ten times. For the more difficult kinds of work, where readings are numerous, or an especially careful regulation of the furnace is desired, this saving is indispensable.

The price paid for the advantage is merely a little attention to the galvanometer sensibility, which may change slightly with temperature, and becomes irregular if faulty contacts are permitted in the circuit. A verification of the sensibility, however, can be made at any time and requires nothing further than to change the potentiometer setting and note the resulting change in deflection.

The galvanometer sensibility should obviously have an integral as well as a constant value. This can readily be secured by varying the scale distance, which is also a convenient way to correct slight

Fig. 2.

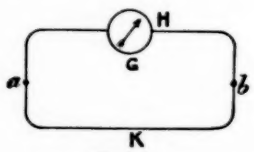

Fig. 3.

Fig. 2. Arrangement of the scale. The numbering is direct, everywhere increasing with increasing E.M.F., yet the reading is zero at the middle of the scale, and readings less than zero are clearly indicated. The figures to the left are, following a common practice, in red, which often shows the direction of a deflection too rapid to permit of reading the numbers.

Fig. 3. To accompany formula 2.

variations in the sensibility. Fig. 2 shows the arrangement of the scale. The method of numbering has some obvious advantages.

Protection against Leakage. — The avoidance of leakage errors is made especially difficult in silicate work by the combination in the furnace of high voltage and poor insulation — the latter due to unavoidable electrolytic conduction at high temperatures.

In order to have leakage affect the galvanometer reading, there must be a failure of insulation in at least two points of the circuit. The law governing the magnitude of the effect may be found as follows:

In Fig. 3, let a and b be the (very high) resistances through which the leakage takes place; let V be the external voltage causing the leak. Let G be the resistance of the galvanometer, and H the remaining resistance which lies with the galvanometer in the circuit

between a and b. Let K be the resistance of the other path from a to b. The total leakage current, L, will equal $V/(a+b)$ and will not be appreciably affected by the relatively small resistances in the circuit. The error caused by L will, however, depend on these resistances. The portion of the current passing through the galvanometer is

$$L\frac{K}{H+K+G}.$$

The resulting error, in microvolts, will be equal to this current divided by the current which is produced by one microvolt, that is:

$$\frac{LK}{H+K+G} \div \frac{1}{H+K+G} = LK = \frac{VK}{a+b} \qquad (2)$$

Leakage errors may therefore be diminished in three ways: *first*, by increasing either a or b, that is, by improving the insulation; *second*, by diminishing the resistance of the alternative path, K;[1] *third*, by diminishing V. This last is the most effective way of removing leakage errors. It can be accomplished by an equipotential shield, a device whose essential features are shown in Fig. 4. The potentiometer, galvanometer, and all other apparatus belonging to the measuring system, are set on metal plates; the leads are completely supported by wires; the plates and the wires are connected so as to form a continuous conductor which is extended into the furnace, where it includes the crucible and also passes between the thermo-element and the furnace cover. This conductor thus interposes between the measuring system and every external electromotive force, while it needs itself but slight insulation in order to be an equipotential surface; the most troublesome leakage, that from the high voltages in the furnaces and elsewhere, is therefore absolutely prevented.[2]

[1] This can often be accomplished by a mere transposition of apparatus, and does not necessarily demand a reduction of the total resistance. The leakage error may obviously be considerably influenced by the mere order in which the different pieces of apparatus stand in the circuit. Formula 2 explains why leakage is sometimes less with potentiometers of low resistance and also shows that this result may be accidental, according to whether the potentiometer resistance is included in the portion K of the circuit. It is always possible, by the method of page 343, to insert resistance so as not to increase the leakage error.

[2] The equipotential shield was suggested by C. T. R. Wilson's electroscope (Proc. Roy. Soc., *68*, 152, 1901). H. P. Brooks has also applied the same principle in a different way to potentiometer work. (Lot. cit.)

The presence of external leakage may be tested by watching the throw of the galvanometer when *both* terminals of the heating circuit are suddenly disconnected. This test is applied from time to time in order to avoid the possibility of error due to accidental contact with or breaks in some part of the shield. If the shield is in

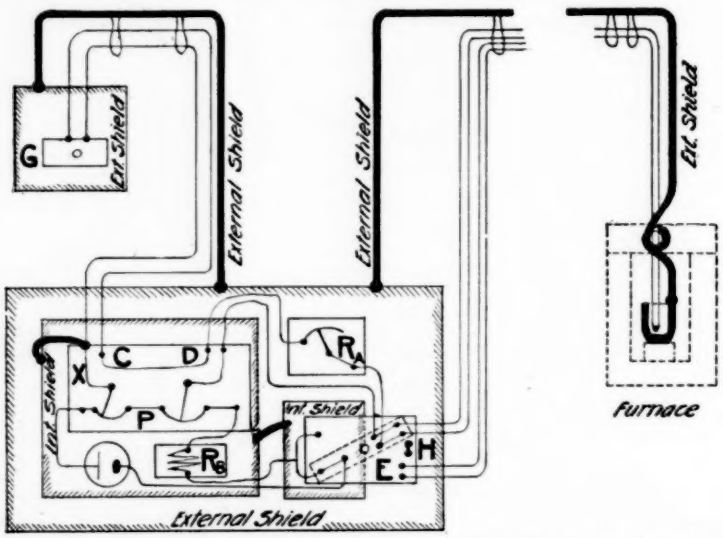

Fig. 4. Very diagrammatic representation, partly in plan, but with the furnace in vertical section, of the measuring apparatus, showing the relations and connections of the two leakage shields. The cold junctions and standard cell are omitted. G, galvanometer, R_A, auxiliary resistance (for adjusting sensibility); R^B, ballast-resistance; P, potentiometer; E, exchanging switch; H, short-circuiting link, for zero adjustment.

perfect condition, of course no external leakage error can possibly occur. As a rule, this test gives zero results during the winter, even in the absence of a shield. This is due to the fact that insulation then fails at but one point in the circuit, and of course does not indicate perfect insulation in the furnace itself.

The use of a complete shield is often inconvenient or impossible. In such cases, a partial shield can be employed, which is connected directly to the potentiometer circuit. Such an arrangement does not prevent the leakage, but guides it to some desired point, thereby reducing the resistance, K, of equation (2). Its effectiveness is more dependent upon good insulation than is that of the complete shield.

Partial shields have been used in three cases: (1) It is sometimes inconvenient to extend the shield into the furnace. By connecting the shield to the thermoelement as near the furnace as possible, K is diminished to the resistance of a few centimeters of the thermoelement wire, and satisfactory results are often obtained. The other cases arise where complete shielding is prevented because the source of leakage is in metallic connection with the circuit. One of these occurs where the voltage or current of a high potential circuit is being measured. The shield is then connected to the junction of the potentiometer circuit and the circuit in question. K is now zero, and the external protection is complete. Another case arises in the protection of the potentiometer system from leakage out of its own storage cell, which we have found by no means negligible in the humid summer months. The arrangement used is as follows:[1] The shield, lying under storage cell, potentiometer and ballast resistance, is connected, as shown in Fig. 4, to the *lower* terminal of the branch circuit, that is, the one nearest an end of the potentiometer wire. This terminal should be

[1] Those especially interested will readily find in the following equations an explanation for the arrangements here described. These equations are obtained by considering that an electromotive force in the leakage path equal and opposite to the normal electromotive force in the circuit between the two ends of that path would reduce the leakage to zero, and therefore, that the current produced by such an electromotive force is equal (but opposite) to the leakage current. The effect of such a current upon the galvanometer is easily calculated. If V is the storage cell voltage (in microvolts), L the leakage resistance, M the fractional portion of the circuit across which leakage occurs, T the resistance of the thermoelement, C the resistance between terminals of the branch (galvanometer) circuit, then the error in microvolts is, for leakage between two points, both in the main circuit, not including C,

$$\frac{VM}{L} MC \tag{3}$$

or two such points, including C between them,

$$\frac{VM}{L} (1 - M)C \tag{4}$$

for leakage from the main circuit to a point between thermoelement and galvanometer, roughly,

$$\frac{VM}{L} T. \tag{5}$$

The efficiency of the above arrangement is dependent upon the small value of the voltage measured. A different disposition would probably be preferable where electromotive forces of the order of 1 volt are to be measured.

made as low as possible, that is, no ballast resistance should intervene between it and the battery. (Ballast resistances are found at this point in some potentiometers. They are, however, objectionable[1] for other reasons, and can easily be short circuited or removed.) The result of this arrangement is that leakage from the battery cannot reach any portion of the circuit outside the apparatus resting on the shield, while within the shield, such leakage as may occur will, in general, produce the minimum amount of error.[2]

Minor Details. — In all refined galvanometer work, provision must be made for eliminating the accidental electromotive forces of the circuit. In thermoelectric work, this requires that the large electromotive forces, those of the thermoelement and battery, be momentarily removed and the circuit then closed. This operation is accomplished by a switch of simple construction, which shifts the terminals of the potentiometer and galvanometer circuit from the thermoelement to a short-circuiting link, and at the same time opens the battery circuit at one point.[3] A further motion of the handle makes connection with a second and a third thermoelement. Provision for the two essential operations, zero adjustment and exchange of thermoelements, is thus made by one simple piece of apparatus. The correction for the accidental electromotive forces is applied by simply adjusting the scale to read zero, and the trouble of making a numerical correction is thus avoided. A slow motion for this

[1] Principally because their presence may restrict the choice of a storage cell to one possessing exceptionally high voltage.

[2] Leakage into the balance resistance is further prevented by suspending this from its own metallic terminals. Such leakage, and also leakage along the potentiometer top from point to point in the circuit, will diminish with the resistance of the potentiometer, and may thus be made negligible. We have no evidence, however, that such leakage in a potentiometer of 10,000 ohms to the volt need be serious. Leakage to the direct junction upon the potentiometer top of thermoelement and galvanometer leads (*CD* in Fig. 4) will be serious only if the resistance of the thermoelement is high (with a constantan element, for instance), and can then be prevented by removing that junction from the potentiometer top altogether.

[3] If this point is near the lower end of the potentiometer — that is, near x in Fig. 4 — leakage at the switch will be prevented while the battery circuit is closed. Trouble from leakage may arise, however, during the zero adjustment, but this can be detected by occasionally disconnecting the other battery terminal. If the regular opening of the battery circuit is at the high end and the two leads are separated from each other and from the rest of the switch by an extension of the internal shield, as indicated in Fig. 4, there will be no danger from leakage at the switch whether the circuit is open or closed.

purpose, sufficiently delicate and entirely free from lost motion, has been found very easy to make. The scale is drawn along against the tension of a coiled spring by winding a cord upon a bent brass rod. Our regular telescopes have a slow motion supplied by the maker.

In this method of compensation it is not the accidental electromotive forces, but the deflection due to them, which is directly compensated, and the adjustment, therefore, is incorrect, if the removal of the thermoelement appreciably changes the resistance of the circuit. This difficulty is inappreciable with platinum thermoelements; with those of constantan, other methods are used.[1]

None of these methods compensates the electromotive forces in the thermoelement leads, and in some portions of the switch itself. All such forces are therefore diminished by making these portions of the circuit entirely of copper. The only exception is the springs and bearing surfaces of the switch, which, for mechanical reasons, are made of manganin, a material at once hard and of small thermoelectric power compared with copper.

The important contacts on the potentiometer are kept in good condition by oiling every few weeks with typewriter oil, in accordance with a suggestion from the Reichsanstalt. A reasonable amount of attention to other contacts in the circuit is also necessary in order to maintain constant galvanometer sensibility.

The cold junctions, protected by glass tubes, are in a bath which is usually maintained at 0° by means of ice. To insure the junctions being at the temperature of the ice, fine copper leading-in wires are used, while oil or paraffin inside the tubes and water outside improve the thermal contact between the ice and the junctions.

[1] A. D. Palmer (PHYS. REV., *21*, 72, 1905) compensates the electromotive forces directly by an auxiliary potentiometer. This method, in the one case where its complication is needed, that is, where the resistance of thermoelement is high, evidently fails unless the galvanometer is at zero on open circuit. Practically, therefore, in employing it, two separate adjustments must be made, of which that on open circuit, with the galvanometer undamped, is somewhat tedious and altogether inadmissible in rapid work. In our laboratory, therefore, another method is employed, and the circuit is closed for zero adjustment through a resistance equal to that of the thermoelement which is then removed from the circuit. The value of this resistance evidently need be only approximate, but it must be so wound as to be free from thermoelectric force — a condition easily realized.

The constancy of the storage cells is increased by shielding them from temperature changes with a wrapping of cotton wool.

Insulation of the standard cells is promoted by suspending them from their own leads.

Since the zero adjustments, as well as the readings, are made on a closed circuit whose resistance is kept constant, the galvanometer is adjusted so as to be damped entirely by the reaction of the circuit, and maximum sensibility is thus obtained. To insure proper damping while the circuit resistance is increased during the comparison of storage and standard cell, a coil is connected between appropriate terminals of the standard cell and galvanometer, This coil has no effect except when the cell is connected to the potentiometer. It then acts as a shunt to the galvanometer, giving critical damping together with a decrease (here unobjectionable) in sensibility.

The galvanometers are placed upon Julius suspensions, which are enclosed against air currents. We have found that the position of the center of gravity with reference to the galvanometer head does not appreciably influence the steadiness, that is, the oscillations which the supports perform about their centers of gravity are not of a character to affect our moving coil galvanometers.

Galvanometer Requirements. — A satisfactory adjustment of the potentiometer system, according to the methods above described, requires a galvanometer which, while not necessarily of extraordinary quality, is well adapted to its work. Leading instrument makers, in this country at any rate, will, as far as possible, furnish instruments to meet specified requirements.[1] The necessary or desirable galvanometer constants are as follows:

(*a*) *Sensibility.* — The most convenient method of defining the sensibility of a galvanometer is to give the deflection in millimeters produced by unit current or voltage with the scale distant 1 meter from the mirror. For sensitive instruments, the unit voltage is 1 microvolt. An instrument, then, which gives a millimeter per microvolt at 1 meter's distance has a sensibility equal to 1.

With reasonably good optical arrangements and fair steadiness, a sensibility of .3 is quite sufficient for silicate work. Half a scale

[1] For a more detailed discussion of the problems of galvanometer adjustment, see "Every Day Problems of the Moving Coil Galvanometer," Phys. Rev., *23*, 382, 1906.

division will then correspond to a microvolt, and the scale distance will usually be more than 1 meter. A sensibility of .5, with 1 scale division per microvolt, is a little more desirable, and may be necessary for reading to tenths of microvolts, or with poor optical arrangements.

(*b*) *Period.* — A period of 10″ is sufficient only for the simpler portions of our work, and scarcely satisfactory in those. 5″ is short enough for almost anything, though a still shorter period is often convenient.

(*c*) *Resistance.* — The necessary total resistance of the galvanometer circuit depends largely upon the type of potentiometer. The resistance of platinum thermoelements at different temperatures varies an ohm or more. Hence for sensibility constant to .5 per cent. a total branch circuit resistance of 200 ohms is desirable. For a potentiometer of high resistance whose branch circuit is (as usual) not constant, the total resistance should be 500 ohms or more (see page 338). This requirement is less important if the range of interpolation is small (see page 339).

Satisfactory values, then, are, a sensibility of .3, a period as short as 5″, and a total or critical resistance of 200 ohms, which should be increased to 500 ohms or more with an ordinary high resistance potentiometer. Greater sensibility, greater quickness and higher resistance are more or less in the nature of luxuries. As far as the galvanometer is concerned, these three constants are antagonistic. For a given type of instrument, an increase in one involves a sacrifice of the others. A high resistance potentiometer (10,000 ohms to the volt) may in thermoelectric pyrometry contribute as much as 170 ohms to the galvanometer circuit; with 500 ohms total resistance, then, over 300 may be in the galvanometer alone, a condition which greatly facilitates the attainment of short periods in galvanometers with weak magnets.[1]

We have found no great difficulty in securing the above performance with several different types of galvanometer, although the majority of the instruments now on the market do not seem to permit of anything very much better. With a low resistance potentiometer the reduction of the total resistance to 200 ohms easily

[1] Every Day Problems, etc., pp. 384, 387.

allows, with the same type of instrument, a sensibility of .5 or a period as short as four seconds. A much better galvanometer performance is certainly possible,[1] although it seems worth while to emphasize the fact that such increase, while desirable, is not necessary for most thermoelectric work and would be dearly bought at the cost of even a slight sacrifice of constancy or steadiness, such as is apt to result from too great delicacy of construction. A considerably better performance, however, than the one above described should be attainable along with ample steadiness and constancy.

Either an especially good galvanometer or a low resistance potentiometer, therefore, allows a short period and excellent sensibility. With an ordinary galvanometer and a high resistance potentiometer a satisfactory arrangement can still be obtained, though it requires fair steadiness and good optical arrangements.

The Potentiometers. — Three reasons have been given for desiring potentiometers of low resistance: The internal leakage is less; better results can be obtained with an inferior galvanometer; and especially, the adjustment for constant sensibility is more easily made. This latter advantage is, of course, far more completely secured in a potentiometer with automatically constant branch circuit resistance. In point of fact, a switch potentiometer constructed to have either low resistance or a constant branch circuit may just as well have the other also.[2]

Of far greater importance, however, are ability to set the potentiometer quickly, and freedom from uncertain contacts, which may affect the resistance of the galvanometer branch. In both these respects the slide wire potentiometer is deficient, so much so as to be very unsatisfactory for melting point work. That it takes more time and attention to set a pointer exactly on a mark than to put a switch somewhere upon its appropriate button is perhaps a minor disadvantage, but the time required to wind the drum of a slide wire instrument from one position to another absolutely precludes simultaneous work with two elements differing much in temperature, while the resistance of the sliding contact is, in ordinary instruments, so uncertain as to make constant sensibility impossible. Devices designed to over-

[1] Every Day Problems, p. 388.
[2] Instrumentenkunde, loc. cit.

come this difficulty are at best open to the objection of introducing an additional complication. It may not be superfluous to call attention to the fact that apparatus which under most circumstances would be quite satisfactory, may fail in melting point work, where the demand for certainty of operation is so much greater. A single faulty observation may destroy the value of a thermal curve several hours long, and the frequent readings leave no time to correct even slight or temporary defects in the apparatus.[1]

Hitherto, all-switch instruments have necessarily been made with high resistance on account of the internal contacts at some of the switches. Since the disadvantages of high resistance are small compared to those presented by the slide wire, the older instruments in this laboratory are Wolff potentiometers of 10,000 ohms to the volt.

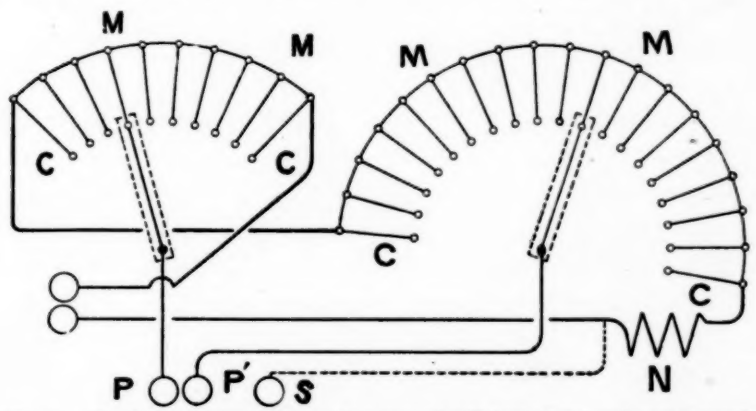

Fig. 5. Simple low resistance potentiometer, of sufficient range, and very convenient for high temperature thermoelectric work. The branch circuit is kept of constant resistance by the coils, *CCC*, and the galvanometer sensibility is therefore constant. *MMN*, main circuit potentiometer coils. *PS*, standard cell connection. A key and a switch are here omitted for simplicity.

There should now be no difficulty in getting all-switch potentiometers possessing not only the low resistance of the slide wire instrument, but a constant branch circuit as well.[2] The slide wire

[1] Much of the difficulty in regard to galvanometer sensibility and contact resistance disappears if the familiar method is adopted of noting the varying times at which regular and integral values of the electromotive forces are reached; but this method is considerably more laborious where one thermoelement is being read, and often inadmissible with two or more.

[2] Instrumentenkunde, loc. cit.

instruments might still have an advantage in the matter of cost, but in this respect also they can be excelled, provided the range of the switch potentiometer is limited to the requirements of thermo-element work. Such an instrument was designed and ordered for this laboratory in April, 1906, and is now in use (Fig. 5). It has only two main switches and measures from 100 to 18,900 microvolts. The coils, *cc*, are so adjusted as to keep the resistance between P and P' always constant. Since the simplest kind of switch will suffice for an instrument of this character, the total cost should hardly exceed that of the coils. Another decade would be desirable,[1] but the advantages of the instrument here figured are believed to be, for melting point work, on the whole superior to those of the usual types. One of these is the possibility of using the instrument as a double potentiometer,[2] a great advantage in work requiring the simultaneous measurement of very different temperatures.[3]

The general usefulness of the resistance thermometer is increased by the fact that ready-made outfits varying in accuracy and elaborateness can be bought for different purposes. For the thermoelement there is at present in commercial instruments practically nothing between the crude, direct-reading voltmeter and the expensive and yet relatively inconvenient five-decade potentiometer with a range of a million microvolts, 98 per cent. of which would never be used. For thermoelectric work, potentiometers of appropriate range may, in spite of their simplicity, be better adapted

[1] And can easily be introduced by the use of a shunted element (Instrumentenkunde, loc. cit.), since with the low range of 18,000 microvolts a single shunted element with a simple switch suffices, and will give an accuracy of .05 microvolt if the switch contact resistance does not exceed .01 ohm.

[2] Instrumentenkunde, loc. cit.

[3] By changing the internal connections of a Wolff 20,000 ohm potentiometer, an instrument of constant galvanometer circuit resistance can be made for thermoelectric ranges; the changes involve a rearrangement of the different *groups* of coils without dividing the group, much less touching the individual coils. There is therefore no danger of injury and the instrument can in a very short time be restored to its original condition if that is desired. In making the readjustment the two higher switches are entirely cut out. The compensating coils of the next two decades are changed from the potentiometer circuit proper to the galvanometer circuit; the result is a three-switch instrument of 5,000 instead of 10,000 ohms to the volt, reading up to 19,980 microvolts by steps of 20 instead of 10 microvolts. In dispensing with the two higher switches one terminal of the standard cell must be permanently connected to the potentiometer circuit, but this connection is in itself a decided advantage.

for measurements of the greatest difficulty and refinement than the existing types, while in instruments where less accuracy is required the simplicity can be correspondingly increased.

Summary.

I. For the most accurate pyrometry, with temperatures up to 1600°, the direct reading pyrometer is not sufficiently sensitive, the resistance thermometer has not sufficient range and is, moreover, too bulky for the best melting-point work. A thermoelement with a potentiometer is the most satisfactory measuring apparatus.

II. The most characteristic requirement in melting-point and calorimetric work at high temperatures is rapidity. This is secured: (*a*) by proper selection and arrangement of the galvanometer. Periods of five seconds are almost necessary and are readily obtained; (*b*) by the use of switches to exchange thermoelements, adjust zero, etc., (*c*) by relying upon the galvanometer for as much of the reading as possible, so as to minimize potentiometer manipulation. For this, constant galvanometer sensibility, and therefore constant resistance in the branch circuit of the potentiometer, is needed. An adjusting rheostat in the circuit secures this result fairly well for ordinary potentiometers, whose branch circuit resistance is variable.

III. External leakage can be absolutely prevented and internal leakage greatly diminished by equipotential shields, which interpose a continuous metallic surface between the circuit and the source of disturbance. Internal leakage also decreases with the resistance of the potentiometer.

IV. The constancy of the potentiometer storage cell is increased by a wrapping which protects it from temperature changes. For some other minor devices, those interested are referred to the body of the article.

V. With galvanometers of familiar commercial types, a sufficiently short period, five seconds, with satisfactory critical resistance and sensibility, can be obtained with a high resistance potentiometer. Either an especially good galvanometer or potentiometer of low resistance makes possible a somewhat better adjustment.

VI. A slide wire potentiometer is very undesirable in rapid work, and especially in melting-point and calorimetric determinations.

VII. By confining the range of the potentiometer to that actually needed in thermoelectric work, an instrument of almost ideal convenience and usefulness can be obtained at relatively low cost. It has constant galvanometer sensibility, low resistance, and ease of manipulation, and can be used on two circuits alternately without resetting.

GEOPHYSICAL LABORATORY,
CARNEGIE INSTITUTION OF WASHINGTON,
June 3, 1907.

THE THERMOELECTRIC BEHAVIOR OF METALS IN SOLUTIONS OF THEIR OWN SALTS.

II. Cadmium Amalgam in a Solution of Cadmium Sulphate.

By William D. Henderson.

Introduction.

THE present paper is the second in a series on the thermoelectric behavior of metals in solutions of their own salts. Paper I.[1] deals with the thermoelectric behavior of silver. The work herein recorded has to do with the thermoelectric behavior of cadmium amalgam in a solution of cadmium sulphate.

The object of this work is in general, an investigation of the relation of heat to electromotive force. The solution of this problem demands the specific investigation of the thermoelectric behavior of a large number of metals, with respect to the direction and magnitude of the thermoelectromotive force under given conditions, and to the relation of this electromotive force to the concentration of the electrolyte. The problem also involves a study of the subjects of osmotic pressure and solution pressure and allied topics, in so far as these forces play any rôle in the production of an electromotive force.

In pursuing the present investigation three specific objects have been kept in view, as follows: First, to determine the direction of the thermoelectromotive force of cadmium amalgam in a solution of cadmium sulphate; second, to determine the relation between the thermoelectromotive force and the concentration of the electrolyte; and third, to compare the thermoelectromotive force due to a given difference of temperature, with the electromotive force due to a corresponding difference of concentration.

When two electrodes of a given metal are immersed in a neutral solution of a salt of this metal, two causes may operate to produce

[1] Physical Review, Vol. XXIII., 2, August, 1906.

an electromotive force. A difference of temperature at the electrodes will produce an E.M.F., commonly spoken of as a thermo-electromotive force. Also, a difference of concentration of the electrolyte will produce an E.M.F., which for the sake of convenience and clearness is sometimes referred to as a concentration-electromotive force. Whether these two electromotive forces are due to one and the same cause remains to be seen.

The apparatus used was very similar to that employed in the investigation on silver (Paper I.), and is shown in outline in Fig. 1. The letters A_1 and A_2, as used in the figure, are employed to designate (*a*) the two legs of the cell, (*b*) the electrodes, or (*c*) the elecrolyte contained therein.

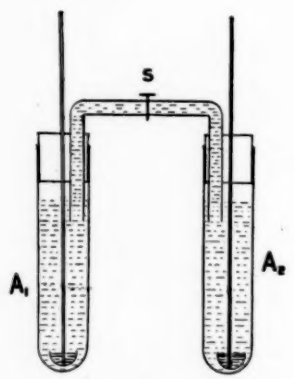

Fig. 1.

Fig. 2.

The electrodes were prepared as shown in Fig. 2. A glass tube (*a*) was sealed into the bottom of a small glass cup (*b*), about 2 cm. in diameter, and 2.5 cm. in depth. Into the tube (*a*), near the bottom, was sealed a short piece of platinum wire (*c*). Tube (*a*) was then filled with cadmium amalgam. Finally, cup (*b*) after being thoroughly cleaned and dried, was filled with the amalgam under test, after which the entire cell was set up as shown in Fig. 1. The siphon which connects the two legs of the cell was provided with a stopcock (*s*).

Temperatures ranging from 0° to 30° centigrade were employed. The lower temperatures, those near 0°, were obtained by means of crushed ice placed in a large Dewar flask. Those of 25° and 30°

were obtained by means of a thermostat which held constant to within a few hundredths of a degree for days. Beckmann thermometers were used, for the most part.

E.M.F. readings were made by means of an Otto Wolff potentiometer, reading directly to 0.00001 volt.

The electrolyte was prepared by dissolving cadmium sulphate, recrystallized from Kahlbaum's C.P. salt, in water redistilled for conductivity purposes.

The cadmium amalgam was of twelve and one half per cent. strength, prepared by dissolving pure cadmium in redistilled mercury, in the ratio of one part by weight of cadmium to seven parts by weight of mercury.

The method of conducting a test was as follows: A solution of $CdSO_4$, or a series of solutions as required, of the desired concentration was prepared as described. Enough amalgam was prepared so that for each test a fresh portion of the amalgam might be used. The electrode cups were cleaned in nitric acid, then washed with distilled water and dried. The amalgam was heated over a water bath until it came to a fluid state, after which the desired amount was transferred to the electrode cups by means of a pipette. The electrodes were then placed in the legs of the cell, and the electrolyte added. The siphon (s) was filled, and finally the entire cell adjusted as shown in Fig. 1. At the close of the test the cell was dismantled, and the entire operation then repeated for a new test, as just described.

Direction of the Thermoelectromotive Force.

The object here was to determine the direction of the thermoelectromotive force of a cell of the type, Cd Am. — $CdSO_4$ — Cd Am., the temperature of electrode A_1 being kept at 0°, and that of A_2, at 30°. The electrolyte was of the same concentration at both electrodes.

It was observed that cadmium amalgam when placed in a dilute solution of $CdSO_4$ loses, after a time, its bright metallic appearance, the surface becoming covered with a grayish colored film. It therefore seemed desirable to make a "time test" of a Cd Am. — $CdSO_4$ thermoelement, to determine how far this film affects the E.M.F.

Two such time tests were made. In the first, a cell of the form shown in Fig. 1 was used. The time was relatively short, readings being taken every ten minutes for an hour and a half. The electrodes A_1 and A_2 were maintained at a difference of temperature $(T_1 - T_2)$ of 29.95°. In half an hour the thermoelectromotive force rose to 0.01175 volt, and this value remained unchanged for the following hour, during which readings were taken. Three hours later the cell showed an increase of only 0.00004 volt.

For the second time test a cell similar to that described in detail in Paper I. was set up. A glass tube, about 5 cm. in diameter and 70 cm. in length, sealed off at one end, was filled with a tenth molecular solution of $CdSO_4$, and was set up vertically in such a manner that the lower half of the tube was contained in an ice bath, and the upper half in a water bath at 30°. One electrode was placed at the bottom of the cell, the other at the top. The difference of temperature of the electrodes was, therefore, equal to the difference of temperature between the ice bath and the water bath.

This test extended over a period of ten days. The results, as tabulated in Table I., show (*a*) that the E.M.F. is directed, in the external circuit, from the warm electrode to the cold — that is, the warm electrode is the cathode; and (*b*) the E.M.F. increases slightly with the time, due probably to the film mentioned. It must be noted, however, that this increase, over a period of ten days, was only 0.00033 volt.

TABLE I.

Time in Hours.	$T_1 - T_2$.	E.M.F. in Volts.	Time in Hours.	$T_1 - T_2$.	E.M.F. in Volts.
0	30.00°	0.00006	106	29.96°	1173
27	30.00	0.01162	118	29.99	1174
32	30.00	1163	123	30.02	1175
37	30.00	1162	142	29.98	1173
47	30.00	1163	154	29.96	1175
58	30.00	1164	174	30.00	1179
75	30.00	1172	192	29.95	1183
80	29.97	1173	214	29.95	1182
94	29.96	1172	220	29.96	1194
99	30.01	1176	244	29.96	1195

Relation of the Thermoelectromotive Force to the Concentration of the Electrolyte.

For this test a series of solutions was prepared having the following concentrations: $n/80$, $n/40$, $n/20$, $n/10$, $n/5$. A normal solution as here used, means a gram molecule of the salt dissolved in one liter of water. The method pursued was as follows: The electrode cups (*b*, Fig. 2) were filled with cadmium amalgam, and then adjusted in the cell, as previously described. The eightieth normal solution ($n/80$) was used first. Electrode A_1 was placed in the ice bath; and A_2 in the 30° bath. The E.M.F. rapidly rose to a constant value, which was recorded.

The electrolyte was now removed and the cell washed and dried. The amalgam was also removed from the electrode cups, which were cleaned and dried, after which a fresh portion of the amalgam was added. A solution of the next higher concentration was then tested.

Table II.

Con.	n/80	n/40	n/20	n/10	n/5
T.E.M.F.	0.01024	0.01070	0.01107	0.01142	0.01172
"	1040	1081	1116	1148	1176
"	1029	1080	1111	1148	1175
"	1028	1083	1111	—	1173

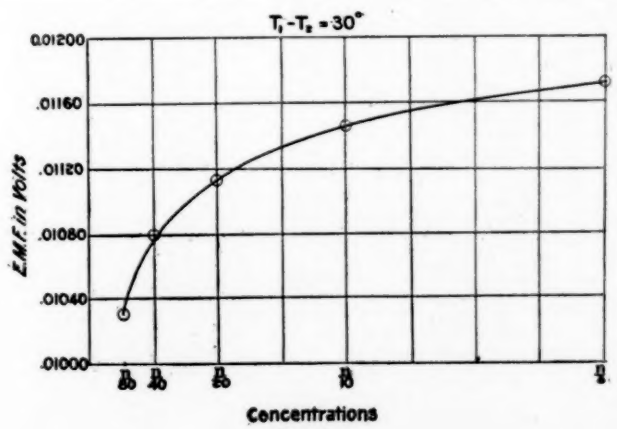

Fig. 3.

Four series of readings were made, a record of which is given in Table II., and the corresponding curve in Fig. 3. Table II., which

shows an excellent agreement between the E.M.F. readings, indicates, together with the curve of Fig. 3, that the thermoelectromotive force *increases* with the concentration of the electrolyte.

COMPARISON OF THE E.M.F. DUE TO A GIVEN DIFFERENCE OF ABSOLUTE TEMPERATURE, WITH THE E.M.F. DUE TO A CORRESPONDING DIFFERENCE OF CONCENTRATION.

The object and conditions of the experiment were as follows: The entire cell was filled with a given solution, $n/10$ say, and the electrodes subjected to a difference of temperature of 30°, which produced a given E.M.F. The ratio of T_2/T_1, measured on the absolute scale, was therefore, in this case equal to $303/273 = 1.11$.

Now it was desired to find what E.M.F., would be produced by a corresponding concentration ratio — that is $C_2/C_1 = 1.11$, the temperature of both electrodes being the same. To obtain the electromotive force due to this concentration ratio it was determined to plot two E.M.F. curves, obtained by different methods, such that one would serve as a check on the other. The two methods of procedure and the results are given in the following paragraph.

First Method. — A series of solutions of $CdSO_4$ was prepared, having the following concentrations: $5n/100$, $8n/100$, $10n/100$, $12n/100$, $15n/100$, $20n/100$. These particular concentrations were chosen, (*a*) because they gave a range which included the tenth molecular solution selected as a standard, and (*b*) because accurately calibrated pipettes capable of producing this series, were available.

One leg of the cell was filled with $10n/100$ solution and placed in the 30° bath. The concentration of this solution was unchanged throughout the experiment. The other leg of the cell was placed in the ice bath. The concentration of the electrolyte in this (the cold) portion of the cell was varied from $5n/100$ to $20n/100$.

To begin with, the E.M.F. of the cell was directed, in the external circuit, from the warm electrode to the cold electrode. It is evident therefore that the effect of increasing the concentration at the cold electrode would be to produce a counter E.M.F., which at a certain point would just balance the thermoelectromotive force. It is evident, also that the cell was operated both as a thermoelement and a concentration element at the same time, except at the

point at which the concentration at both electrodes became the same ($n/10$), at which instant the cell was functioning as a thermoelement only.

A record of the experiment is contained in Table III.

TABLE III.

T_1-T_2	C. of Warm El.	C. of Cold El.	E.M.F.
30.02	$10n/100$	$5n/100$	0.01690
30.01	"	8/100	1352
30.02	"	10/100	1187
29.98	"	12/100	1072
30.00	"	15/100	905
30.00	"	20/100	738

Second Method. — The experiment was now repeated, though in a somewhat modified form, in order to obtain a second E.M.F. curve to serve as a check on the first.

The entire cell was placed in the 30° bath, both electrodes being therefore at the same temperature. The concentration of the electrolyte A_1 was held at $10n/100$ throughout the experiment. The concentration of A_2 was varied from $5n/100$ to $20n/100$ as before. In this case the element was operated purely as a concentration cell.

The results of this series of tests are given in Table IV.

TABLE IV.

T_1-T_2	C. of A_1.	C. of A_2.	E.M.F.
0.0	$10n/100$	$5n/100$	+0.00540
0.0	"	8/100	246
0.0	"	10/100	4
0.0	"	12/100	−0.00104
0.0	"	15/100	291
0.0	"	20/100	460

If now the concentrations be plotted as abscissas and the E.M.F. readings as ordinates, Tables III. and IV. give a pair of E.M.F. curves which theoretically should coincide when drawn with reference to x-axes 1,187 units apart.

Fig. 4 shows such a combination of E.M.F. curves. The continuous line represents E.M.F. readings due to both a difference of

temperature and concentration, as given in Table III. The curve represented by the broken line is taken from the data given in Table

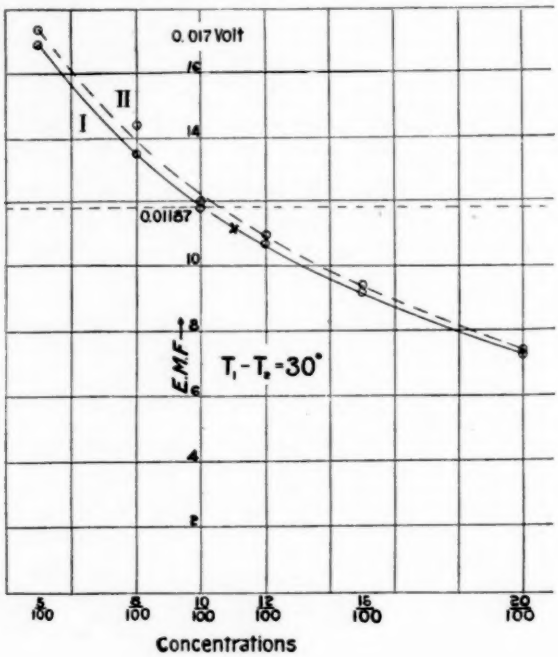

Fig. 4.

IV., and is drawn with reference to the x-axis indicated by the horizontal dotted line.

The point (x) on curve I is the point at which the concentration ratio $C_2/C_1 = 1.11$ might be expected to produce an E.M.F. equal to that resulting from the absolute temperature ratio, $T_2/T_1 = 1.11$.

It will be noted, however, that there is at this point on the curve an outstanding E.M.F. of over 0.01100 volt. That is to say, a a difference of concentration represented by the ratio $C_2/C_1 = 1.11$ will produce an E.M.F. equal to 0.00128 volt; while, on the other hand, corresponding difference of absolute temperature ($T_2/T_1 = 1.11$) will produce an E.M.F. equal to 0.01187 volt, a value nearly ten times as great.

SUMMARY.

1. Cadmium amalgam in a solution of cadmium sulphate gives between 0° and 30°, a themoelectromotive force directed, in the

external circuit, from the warm electrode to the cold — that is, the warm electrode in the cathode. It was shown in Paper I. that in the case of silver the conditions are just the opposite, the *cold* electrode being the cathode. Further, with cadmium amalgam, the thermoelectromotive force is relatively constant, and for given concentrations is reproducible.

2. The thermoelectromotive force is a function not only of the temperature but also of the concentration of the electrolyte, an increase in concentration producing an increase of E.M.F. In the case of silver, the conditions are again reversed, an increase in concentration of the electrolyte producing a decrease of E.M.F.

3. Within a range of temperature from 0° to 30°, the thermoelectromotive force due to a given difference of absolute temperature is nearly ten times as great as the E.M.F. due to a corresponding difference of concentration. It therefore follows that the thermoelectromotive force observed cannot be accounted for on the assumption of an increase of osmotic pressure, since according to the theory a given increase of osmotic pressure due to a given difference of absolute temperature should be equal to that due to a corresponding difference of concentration. Nor can we well assign the large outstanding E.M.F., shown in Fig. 4, to a change of solution tension in the cadmium amalgam, unless we are willing to assume, since the warm electrode is the cathode, that the solution pressure of the metal *decreases* with an *increase of temperature*.

UNIVERSITY OF MICHIGAN,
May 20, 1907.

STUDIES IN LUMINESCENCE.

BY EDWARD L. NICHOLS AND ERNEST MERRITT.

VIII. THE INFLUENCE OF THE RED AND INFRA-RED RAYS UPON THE PHOTOLUMINESCENCE OF SIDOT BLENDE.

THE effect of the red and infra-red rays in suppressing the phosphorescence of various substances has long been known,[1] and has frequently been utilized in the study of the infra-red spectrum. The effect is exhibited by Sidot blende more strongly perhaps than by any of the other phosphorescent sulphides. In the preceding paper of this series[2] we have called attention to another effect produced by the longer waves, namely the restoration of a screen of Sidot blende, after the excitation and complete decay of phosphorescence, to a standard condition, so that the result of a subsequent excitation shall be unaffected by the previous history of the substance. While this new effect is doubtless connected in some way with that first mentioned, the nature of the relationship between the two is by no means clear. For this reason, and because of the bearing of the phenomena upon the general theory of luminescence, we have investigated the influence of the longer waves upon the luminescence of Sidot blende under a variety of different conditions. The experiments to be described in the present paper were made during the progress of work upon the luminescence of Sidot blende that has already been published, and have extended over a period of about three years. While there are certain parts of the work where additional investigation is much to be desired, it has seemed inadvisable to postpone longer the publication of the results thus far obtained, since the experimental work has been interrupted and cannot be taken up again for some months.

[1] References to the literature of the subject are given by Dahms, Annalen der Physik, Vol 13, p. 425.

[2] Further Experiments on the Decay of Phosphorescence, PHYSICAL REVIEW, Vol. 23, p. 37, 1906.

The work naturally falls under several heads as follows:

1. The effect upon the luminescence of Sidot blende of exposure to the longer waves *before* excitation.

2. The effect of the longer waves *during* excitation.

3. The effect of the longer waves *after* excitation, *i. e.*, during the decay of phosphorescence.

4. The influence upon the effect studied of the wave-length of the red and infra-red rays used.

1. The Effect of the Longer Waves Before Excitation.

Experiments described in the preceding paper of this series have shown that when Sidot blende is excited to luminescence "some change is produced in the material by the action of the exciting light, and that this change persists for a considerable period after all visible phosphoresence has ceased. In other words the effect of a given excitation in producing phosphorescence depends upon the previous history of the phosphorescent substance. If the screen is allowed to rest in the dark for a number of hours this semi-perma-

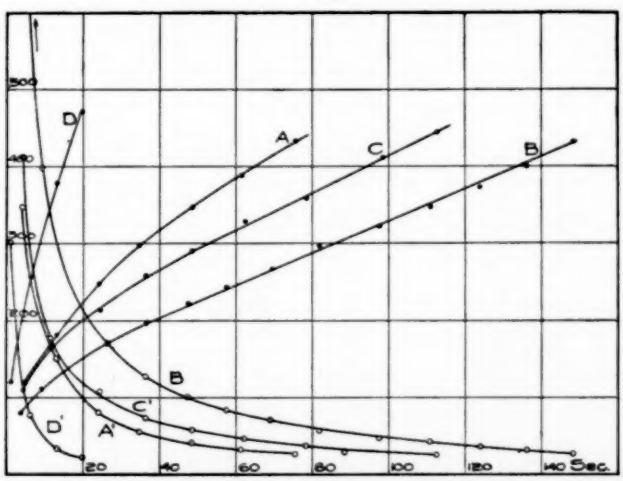

Fig. 42. Illustrating the relative effect of rest and of exposure to infra-red.

A, 10 sec. excitation after rest of 24 hours in the dark.

B, 2 min. excitation.

C, 10 sec. excitation immediately after *B*.

D, 10 sec. excitation after exposure of 4 min. to infra-red from 50 candle power lam p

Curves *A'*, *B'*, *C'*, *D'* correspond to *A*, *B*, *C*, *D* except that *I* is plotted in place of $I-\frac{1}{}$.

nent effect of exposure in part dies out. But rest alone does not restore the screen completely even if continued for several days." An exposure of a few seconds to the rays from a 50 c.p. lamp seen through ruby glass is however sufficient to restore the screen to what seems to be a definite standard condition.

The phenomenon in question is well illustrated by the curves of Fig. 42, which is reproduced from our last article. If we compare curves *A*, *C* and *D*, all corresponding to the same excitation, it is clear that exposure to the longer waves *before excitation* exerts a very marked influence upon the rate at which the phosphorescence, excited after this exposure, will decay. While the semi-permanent change produced by excitation is partly lost as the result of prolonged rest in the dark, rest alone is not a very satisfactory means of restoring the substance to a standard condition. Thus a rest of 24 hours brings about a change in the decay curve following a 10-sec. excitation from *C* to *A*. Rest for several days would shift the curve somewhat further to the left. But even a rest of several weeks failed to bring the decay curve as far to the left as curve *D*.

Curve *D*, Fig. 42, was taken after an exposure of four minutes to the longer waves. A very much shorter exposure would have been

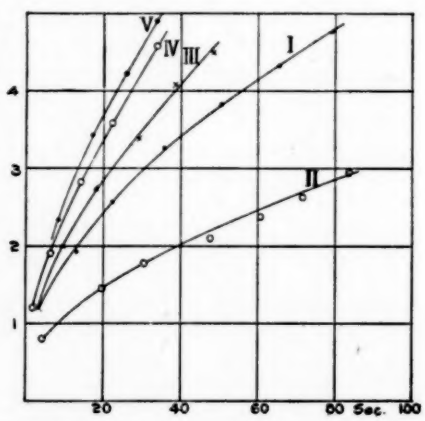

Fig. 55. Effect on the decay curve of exposure to the infra-red for different times.
Curve I. 10 sec. exposure after 48 hrs. rest in the dark.
Curve II. 2 min. exposure.
Curve III. 10 sec. exposure after 1 sec. infra-red.
Curve IV. 10 sec. exposure after 3 sec. infra-red.
Curve V. 10 sec. exposure after 60 sec. infra-red.

nearly, if not quite, as effective. This point is brought out by the curves of Fig. 55, which were taken to determine the way in which the effect depended upon the duration of exposure to the longer waves. In taking these curves the procedure was as follows: In each case the screen was first exposed for two minutes to the mercury arc; the phosphorescence was then allowed to decay for two minutes, at the end of which time, while still visible, it was too faint for measurement. The screen was then exposed to the rays of a 50 c.p. lamp at a distance of 5 inches, a piece of ruby glass being interposed between the lamp and the screen; the duration of this exposure was 1 sec. for Curve III., 3 sec. for Curve IV., and 60 sec. for Curve V. After this exposure to the longer waves the screen was excited by the mercury arc for 10 sec., and the decay curves shown in Fig. 55 were observed by the procedure described in our last paper.

It will be observed that even an exposure of only 1 sec. is more effective than 48 hours' rest. It will be noticed also that 3 sec. exposure to the longer waves is nearly as effective as an exposure of a minute.

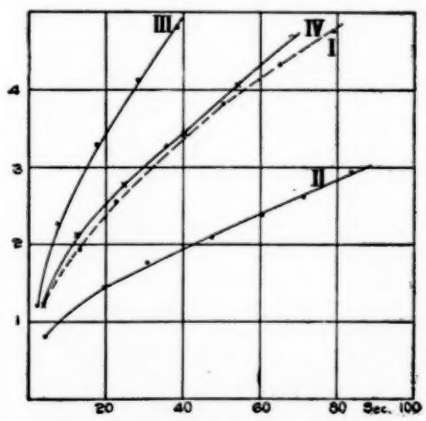

Fig. 56. Effect on the decay curve of exposure to the infra-red for different times. The intensity of the infra-red rays was here only about $\frac{1}{3}\frac{1}{5}$ of the intensity used for the curves of Fig. 55.

Curve I. 10 sec. exposure after 48 hrs. rest in the dark.
Curve II. 2 min. exposure.
Curve III. 10 sec. exposure after 60 sec. infra-red.
Curve IV. 10 sec. exposure after 15 sec. infra-red.

With red and infra-red rays of less intensity a longer time is required to destroy the effect of previous excitation. The curves of

Fig. 56 were taken with a procedure similar to that for Fig. 55, except that the distance of the 50 c.p. lamp from the Sidot blende screen was 30 inches instead of 5 inches. Exposure for 60 seconds to these less intense rays produces as great an effect as a similar exposure to the stronger rays. But this is not true for shorter exposures. While the ultimate effect of the weaker rays is apparently the same, more time is required to produce the change when the rays are of small intensity; approximately, at least, the change produced depends upon the product of intensity and duration of exposure.

The experimental data bearing upon this phase of the subject are so meager as to permit of only the most general conclusions, and additional experiments are much to be desired. So far as they go however the results indicate that the condition in which the material is left after the excitation and decay of phosphorescence is an unstable one, due perhaps to some new grouping of the molecules of the phosphorescent material. During rest in the dark accidental disturbances of various kinds may cause the substance to return more or less completely to its normal condition. The effect of rest is therefore uncertain, depending as it does upon the extent to which various obscure and perhaps unrecognized agencies are active. Certain waves, however, lying chiefly in the infra-red region of the spectrum, have a definite and positive effect in restoring the substance to its normal condition.

Influence of the Longer Waves During Excitation.

We have seen that a condition is developed in Sidot blende by excitation which is favorable to the production of strong luminescence by a subsequent excitation. A long excitation is therefore more effective than exposure to equally intense exciting rays for a shorter period; for the favorable condition developed in the early stages of excitation makes the exciting rays that act later more effective. The luminescence of such a substance during excitation — *i. e.*, the fluorescence — will be relatively weak when excitation first begins and will increase in intensity as the exposure continues, reaching a steady value only after a considerable time. In Sidot blende, with the exciting light used in most of our experiments, three or four minutes were required to reach a steady value.[1]

[1] See the preceding paper of this series, *l. c.*

The steady condition finally reached is manifestly characterized by equality in the rates of development and decay of the condition favorable to luminescence to which we have just referred. If we think of this favorable condition as being due to some new grouping of the molecules, then the condition of steady fluorescence is reached when these favorable groups are being broken up, either spontaneously or through the action of some outside agent, just as rapidly as they are formed by the action of the exciting light.

It is clear that the intensity of steady fluorescence will be made less by any agent which increases the rate at which the assumed favorable grouping is destroyed. Now it is precisely this effect that is exerted by the red and infra-red rays; and we should therefore anticipate that the fluorescence of Sidot blende would be diminished by the action of the longer rays.

This effect of the longer waves, which does not appear to have attracted much attention heretofore, may readily be made very marked indeed. Thus the rays from a projecting lantern after passing through a sheet of hard rubber 0.2 mm. thick are able to reduce the fluorescence of Sidot blende so greatly as to leave the intensity only a few per cent. of its normal value, and this too with very intense excitation. If the ultra-violet rays of a spark are used for excitation numerous lecture experiments may be devised for demonstrating the existence of the invisible rays at the two ends of the spectrum. As compared with the experiments first proposed by Dahms, in which the effect of the infra-red rays upon phosphorescence is utilized, this procedure has the advantage of giving a persistent rather than a fleeting effect.

In studying the influence of the longer rays upon fluorescence we have directed our attention especially to the distribution of the effect throughout the fluorescence spectrum. While the result of exposure to longer waves is to unquestionably diminish greatly the *total* brightness of the fluorescence light, it might be that in certain restricted regions of the spectrum the intensity would be increased rather than diminished, or at least that the effect of the infra-red rays would vary greatly in magnitude in different parts of the fluorescence spectrum.

For the work on this phase of the subject the Sidot blende screen

was mounted in front of a Lummer-Brodhun spectrophotometer, with an acetylene flame as a comparison source as in our previous work. The infra-red rays from an arc fell upon the screen after passing through hard rubber. The intensity of fluorescence was then measured in different parts of the spectrum, first with, and then without the action of the longer waves, the excitation remaining constant. As exciting source a mercury vapor lamp was first used, the lamp being made of the so called "Uviol" glass, which possesses an unusual transparency to the ultra-violet rays.

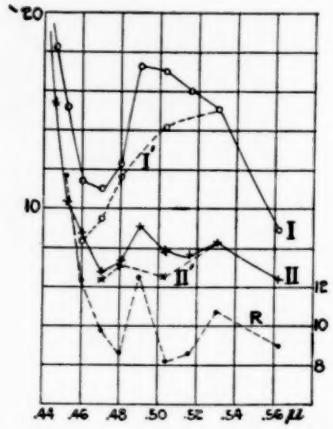

Fig. 57. Effect of infra-red on fluorescence. Sidot blend excited by "uviol" mercury vapor lamp.

Curve I. Fluorescence spectrum.

Curve II. Fluorescence spectrum when the screen is exposed to infra-red during excitation.

Curve I.′ Fluorescence spectrum with plate glass between screen and mercury lamp.

Curve II.′ Same as I.′ except that screen is also exposed to infra-red.

Curve *R*. Reflection of exciting light from white surface.

In Fig. 57, Curve I. shows the ordinary fluorescence spectrum of Sidot blende produced by the mercury lamp, while Curve II. shows the spectrum as modified by exposure to the infra-red. In the case of Curves I.′ and II.′ a sheet of ordinary glass was interposed between the lamp and the screen, so that the ultra-violet rays were in large part removed from the exciting light. It is clear that the ultra-violet-rays of the Uviol lamp introduce a band at about .49 μ which overlaps and distorts in an annoying way the usual green band at 0.51 μ.

A more annoying source of disturbance in these experiments, however, was the light reflected from the screen, which was mixed with fluorescence light and practically inseparable from it. By making observations only at points lying between the bright lines of the mercury spectrum we had expected to be untroubled by reflected light. But owing either to optical imperfections in the apparatus or to the existence of a faint continuous spectrum in the light from the lamp, there was always enough reflected light in the field of

the spectrophotometer to be an important and disturbing factor. To get some idea of the intensity and distribution of this reflected light we made the observations plotted as Curve *R* in Fig. 57 with a screen of MgO on cardboard instead of the Sidot blende screen. To avoid confusion this curve is displaced downward in the plot. The intensity for points on Curve *R* should be read from the right hand side of the figure.

The irregular distribution of the reflected light and the great uncertainty in its measurement make the experiments plotted in Fig. 57 of little quantitative value. Especially is this true for the violet end of the spectrum, where the reflected rays are of great intensity. We could not even feel sure that the longer waves produced any effect at all in this region.

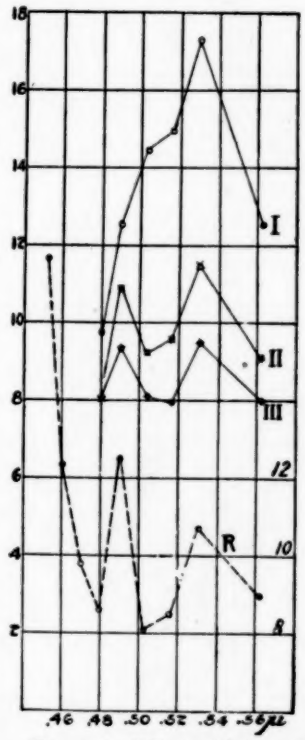

Fig. 58. Effect of infra-red on the fluorescence of "Emanationspulver," excited by the uviol lamp.

With a different zinc sulphide screen, the so called "Emanations pulver" referred to in the foregoing paper of this series, the conditions were somewhat more favorable. The curves in Fig. 58 show the ordinary fluorescence spectrum (Curve I.); the fluorescence spectrum with exposure to weak infra-red rays (Curve II.); the fluorescence spectrum during exposure to strong infra-red rays (Curve III.); and the reflected light determined as before. Different intensities of infra-red were obtained by using in one case one piece of black rubber and in the other case two pieces between the arc lamp and the screen. By this procedure it is possible to determine the *ratio* of the effects produced by strong and weak infra-red, in spite of the uncertainty in the value of the reflected light. Thus the difference between the ordinate of Curve I. and the corresponding ordinate of Curve II. is a measure of the effect produced by weak infra-red; reflected light, since it affects

both measurements, is eliminated by taking their difference. Similarly the difference between the ordinates of Curves II. and III. measures the effect of the stronger infra-red. It is interesting to note that the ratio of these effects is nearly constant throughout the green band. Beginning at 0.562 μ and running toward the violet the ratio has the values: 1.32, 1.36, 1.31, 1.22, 1.94. Except for the last point, which is so near the edge of the band that the intensity of fluorescence is small, the values are constant to within observational errors. This fact adds another to the many that have been observed in the course of our work on luminescence to indicate that each band in a luminescence spectrum behaves as a unit — that whatever affects one part of the band affects all other parts of the band in the same proportion.

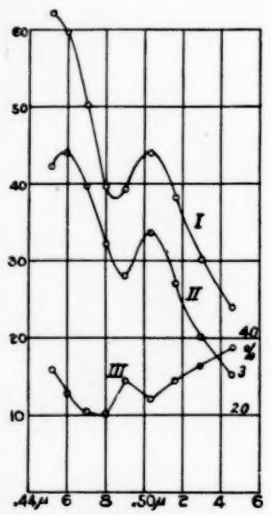

Fig. 59. Effect of infra-red upon the fluorescence of "Emanationspulver" excited by the ultra-violet rays of an iron spark.

In some ways the most satisfactory method of studying the effect in question is to use only ultra-violet light in excitation. All troubles due to reflected light are in this case removed. The results of this procedure in the case of the original Sidot blende screen used in our earlier experiments are shown in Fig. 59. An iron spark was used as an exciting source, a spectrum being formed by a quartz train and only the ultra-violet rays used. The source of infra-red was an arc lantern whose rays passed through a sheet of hard rubber 0.2 mm. thick. The effect of exposure to longer rays during excitation by the ultra-violet rays of the iron spark was to change the fluorescence spectrum from Curve I. to Curve II. The diminution in intensity brought about by exposure to the longer rays, expressed as a fraction of the ordinary fluorescence at the same wave-length, is given in Curve III.

More extended experiments are required to determine whether the change in the effect from 38 per cent. at 0.546 μ to 20 per cent. at .480 μ is real, or the result of errors. It does not seem likely,

however, that experimental errors alone can account for so great a change. In interpreting the results we must bear in mind the fact that the spectrum shown in Fig. 59 obviously consists of two overlapping bands, and that the infra-red effect may differ for the two. It is highly probable also that still another band is present at 0.49 μ, as was found to be the case with ultra-violet excitation in the experiments plotted in Fig. 57; and for this band the effect of the longer waves may be different still. It is clear that further experiments on this branch of the subject are needed.

Effect of the Longer Waves During Decay.

In studying the effect of the infra-red rays upon the decay of phosphorescence two methods were used. In the first of these the intensity of the total phosphorescent light was measured by a photometer at different times after excitation had ceased, by the same procedure as that described in our last article. The violet end of

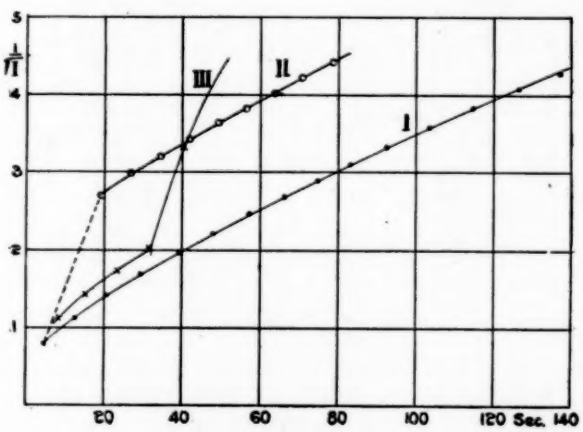

Fig. 60. Influence of exposure to infra-red during decay upon the form of the decay curve.

Curve I. Ordinary decay curve.

Curve II. Screen exposed to infra-red after decay had proceeded for 4 sec. Infra-red cut off at $t = 19$ sec.

Curve III. Screen exposed to infra-red after decay had proceeded for 32 sec.

the carbon arc spectrum was used for excitation, and a 50 c.p. incandescent lamp as a source of infra-red rays. In these experiments a cell containing a solution of iodine in carbon disulphide was used

instead of hard rubber to remove the visible rays. The distance of the lamp from the Sidot blende screen was about 60 cm.

The curves of Figs. 60 and 61 show some of the results obtained by this procedure. In Fig. 60, Curve I. is the ordinary decay curve without exposure to infra-red. In the case of Curve III. the infra-red rays were allowed to fall on the screen when the decay

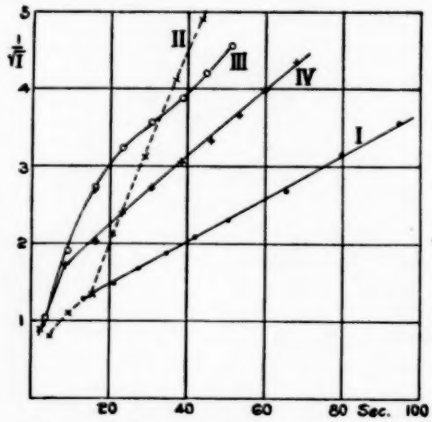

Fig. 61. Influence of exposure to infra-red during decay upon the form of the decay curve.

Curve I. Ordinary decay curve.

Curve II. Screen exposed to infra-red after the decay had proceeded for 18 sec.

Curve III. Screen exposed to infra-red during excitation and for the first 16 sec. of decay.

Curve IV. Screen exposed to infra-red during excitation and for the first 9 sec. of decay.

had proceeded for about 32 sec. In Curve II. the infra-red rays were turned on about 4 sec. after the end of excitation and were cut off again at the end of about 19 sec. The great increase in the rapidity of decay brought about by infra-red rays, even when of such small intensity as those used in these experiments, is clearly shown.

There was no indication in these experiments of any temporary *increase* in the brightness of phosphorescence when the rays were first turned on, as has been noted by many observers in the case of Balmain's paint and other phosphorescent sulphides. Dahms has already called attention to this peculiarity of Sidot blende. The effect of the longer waves in suppressing phosphorescence has sometimes been explained by assuming that these rays act in the same

way as does a rise of temperature; *i. e.*, that they accelerate the process which causes phosphorescence, so as to produce a brief flash, due to the sudden liberation of the energy stored during excitation, followed by a complete loss of luminescence when the stored energy has been used up. While this explanation of the phenomenon may be correct for the other phosphorescent substances it cannot be applied without essential modification to the case of Sidot blende.

Perhaps the most striking feature of the curves in Fig. 60 is the nearly exact parallelism that exists between the later part of Curve III. (after the infra-red rays were cut off) and the straight part of the ordinary decay curve. The action of the longer waves appears to be to bring the material quickly into the same condition as regards ability to emit light that it would have acquired at the end of a much longer period of ordinary decay.

In the case of Curves III. and IV. of Fig. 61 the screen was exposed to infra-red during excitation and during the early stages of decay. The infra-red rays were cut off at the points indicated by the break in the curves. It will be noticed that the latter portion of Curve III. is nearly parallel to the straight part of the ordinary decay curve; but in Curve IV., where the infra-red was cut off earlier, the straight part of the curve is not even approximately parallel to Curve I.

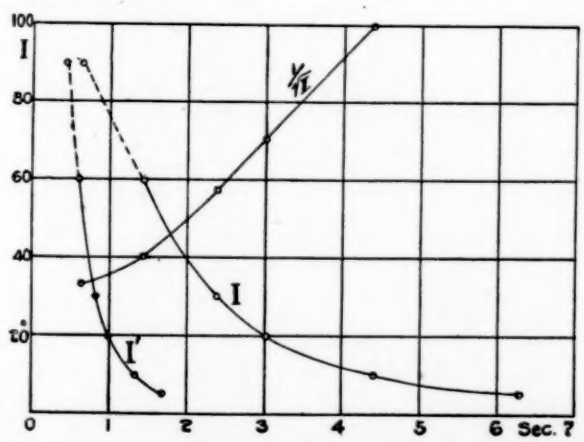

Fig. 62. Influence of exposure to infra-red on form of decay curve.
Curve I. Ordinary decay curve for $\lambda \times 0.497\ \mu$.
Curve II. Screen exposed to infra-red immediately after the end of excitation.

For the early stages of decay a number of curves were taken by means of the spectrophotometer, the method being that described in the fifth and sixth papers of this series.[1] With this method it is impracticable to follow the decay for more than a few seconds, since the illumination of the spectrophotometer field soon becomes too faint for accurate measurements. The method possesses a great advantage, however, in the fact that the effect of the long waves can be determined for different parts of the phosphorescence spectrum.

For the curves shown in Figs. 62 and 63 the exciting light was

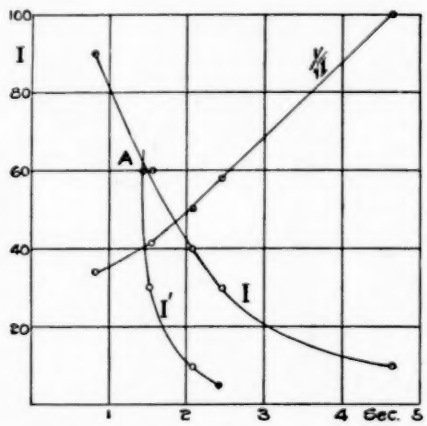

Fig. 63. Curve I. Ordinary decay curve for $\lambda \times 0.497\,\mu$.
Curve II. Screen exposed to infra-red after decay had proceeded to *A*.

the violet of the carbon arc spectrum. For the curves of Figs. 64–67 a spark between cadmium terminals was used in excitation. The intensity of phosphorescence has been plotted in all of these curves instead of the reciprocal square root, although in some cases the latter value has been plotted also. In all these figures the curve marked I. was taken without infra-red[2] and that marked I.′ with infra-red. In general the exposure to infra-red began at the instant the excitation ceased, the shutter being arranged so that the same movement that cut off the exciting rays allowed the infra-red rays to fall upon

[1] PHYSICAL REVIEW, Vol. XXI., p. 247; and Vol. XXII., p. 279.

[2] The carbon arc was used as a source of infra-red, a piece of dense ruby glass serving as a filter. Red light, and perhaps a little yellow light, was therefore present in addition to the infra-red. There has been nothing in our experiments to indicate that the presence of these visible rays modifies the results in any way.

the screen. In the case of Fig. 63 exposure to the infra-red did not begin until about 1.4 sec. after the end of excitation. Numerous

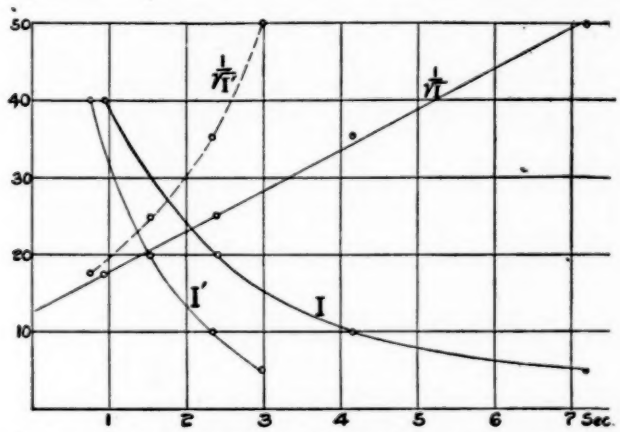

Fig. 64. Decay curves with and without infra-red. $\lambda = 0.546\mu$.

curves of this kind were taken in which the exposure to infra-red began at different times after the beginning of decay. All of these

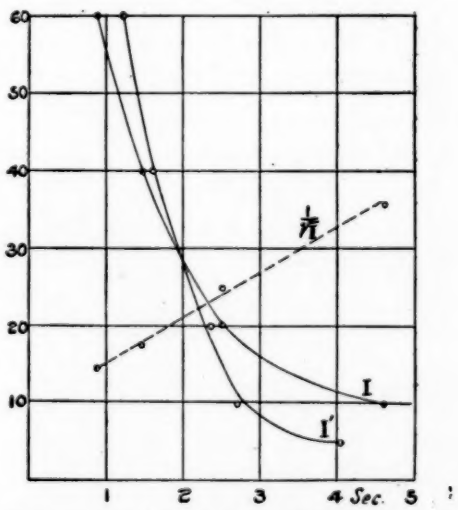

Fig. 65. Decay curves with and without infra-red. $\lambda = 0.474\mu$.

curves show the same sudden drop in intensity at the instant that the long waves begin to act.

The curves of Figs. 62, 63, and 64, except for the method of

plotting, are quite similar to the curves for the total light obtained by the photometer method first described. Apparently the action of the longer waves during the first few seconds of decay is quite similar to its action later. It will be observed that the curves of Figs. 62–64 refer to regions of the phosphorescence spectrum either near the maximum or toward the red edge of the band.

Figs. 65, 66 and 67 show the influence of the longer waves upon those regions of the fluorescence spectrum lying near and beyond the violet edge of the green band. Here the effect seems to be entirely different. At 0.445 μ (Fig. 67) the effect of exposure to infra-red is to retard the decay of phosphorescence instead of to accelerate it. In the region lying between the green band (0.51 μ) and the violet band (0.45 μ) the effect of the infra-red is at first to retard the decay and later to accelerate it (Figs. 65 and 66).

Owing to the faintness of the spectrophotometer field and the rapidity with which the phosphorescence decays it is difficult to determine the form of the curves in the early stages of decay with accuracy. Especially is this true in the blue and violet, owing to the small luminosity of this region of the spectrum. Each point plotted represents however the average of a number of separate readings. For each pair of points the observations for the time of decay with and without infra-red were taken alternately. No special precautions were taken to keep the exciting source constant. The slight initial curvature of the line for $I^{-\frac{1}{2}}$ in Figs. 62 and 63, where the exciting light was from the carbon arc is perhaps to be explained as the result of variations in this source. In the case of the other observations, in which a spark was used in excitation, the points for $I^{-\frac{1}{2}}$ lie reasonably well upon a straight line, and thus give a check upon the accuracy of the observations.

The remarkable reversal in the effect of infra-red in passing through the luminescence spectrum received ample qualitative confirmation. With the spectrophotometer set for some region in the blue or violet the brightness of the field increased noticeably for a few seconds when the screen was exposed to infra-red during decay, even when the exposure first began several seconds after the end of excitation. The same effect was observed in the case of "emanations pulver" and Balmain's paint. In the case of the latter sub-

stance the flash that accompanied exposure to the longer waves developed more slowly and lasted longer than in the case of Sidot blende.

Two interpretations of the results brought out in Figs. 62–67 suggest themselves. Neither, however, is wholly satisfactory.

In all of these experiments the luminescence spectrum consisted of two bands, namely, the green band at 0.51 μ, and the violet band at about 0.45 μ. It is possible that the infra-red rays retard the decay of phosphorescence in the case of the violet band and accelerate it in the case of the green band. In the curves of Fig. 67 we

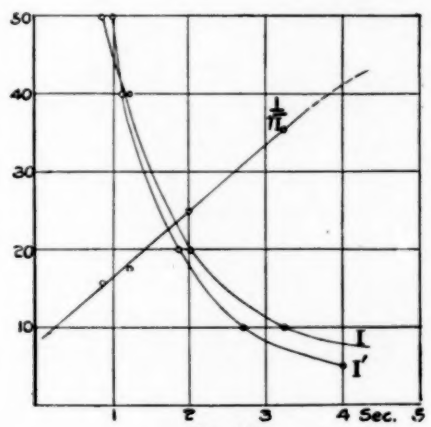

Fig. 66.

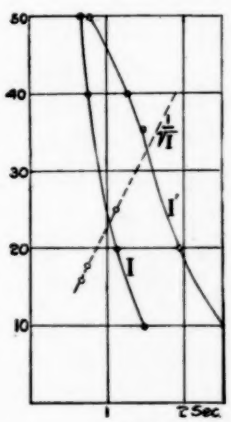

Fig. 67.

Decay curves with and without infra-red. $\lambda = 0.464\mu$ (Fig. 66) and $\lambda = 0.445\mu$ (Fig. 67).

are dealing with the violet band only; in Figs. 62, 63 and 64 the light is almost entirely from the green band; but at wave-lengths 0.474 μ (Fig. 65) and 0.464 μ (Fig. 66) the light entering the collimator slit must be partly from one of these bands and partly from the other. The violet band apparently decays more rapidly than the green band. (Compare the slant of the line for $I^{-\frac{1}{2}}$ in Fig. 67 and Fig. 64.) If the violet band is initially the brighter of the two the retarding effect of the infra-red upon the decay of this band will predominate in the early stages of decay; while later, when the violet band has nearly died out and the light is chiefly due to the green band, the opposite effect will predominate. The two curves I. and I.′ will therefore intersect, as shown in Fig. 65 and Fig. 66.

Two objections may be urged to this explanation. If the light in the case of Figs. 65 and 66 is from two bands that decay at different rates we should hardly expect the relation between t and $I^{-\frac{1}{2}}$ to be as simple as the linear relation that holds for the green band alone. Yet the deviation from a linear relation in both these cases is well within the errors of observation. Again, if the infra-red rays increase the brightness of the violet band after excitation has ceased it would seem reasonable to expect a similar effect during excitation. Yet the effect during excitation (Fig. 59) is practically the same for both bands.

We were first led to expect increased brightness in the violet during exposure to the infra-red, and to undertake experiments in the hope of detecting such an effect, as the result of an entirely different line of reasoning. Looking upon phosphorescence as due to the recombination of ions dissociated by the action of the exciting light, we have explained the fact that the phosphorescence light is of greater wave-length than the exciting light (Stokes' Law) briefly as follows: Dissociation results from the violent resonant vibration of a neutral molecule of the active substance under the influence of the exciting waves. The wave-lengths of maximum resonance and therefore maximum excitation is determined by the natural period of vibration of the active molecule, which is influenced to some extent, but not greatly, by the surrounding solvent. The charged ions resulting from excitation will however be attracted by the neutral molecules of the solvent and will form the nuclei of heavy aggregations of molecules; and recombinations of the ions will therefore occur under conditions which make the resulting vibrations longer, on the whole, than the period of the active molecules before dissociation. Hence the well-known displacement of the luminescence spectrum with reference to the absorption spectrum.

Now the effect of the infra-red rays may be to so shake up the molecules of the solvent as to prevent the loading down of the ions by the attraction of neutral molecules, or to destroy such heavy aggregations if already formed. Under the influence of the infra-red therefore the light emitted will be due largely to the vibrations that occur during the recombination of *unloaded* ions and will be of the same wave-length as that which the active substance absorbs.

If the screen is exposed to infra-red rays after excitation we should expect a decrease in the intensity of phosphorescence throughout the phosphorescence band due to the breaking down of the groups of molecules referred to above. But owing to the resulting increase in the number of unloaded ions we should also expect the emission of light whose wave-length is that of the resonant absorption band of the substance. Now the absorption band always lies on the ultra side of the luminescence band, and usually the two bands overlap. (That this is the case with Sidot blende is evidenced by the fact that this is one of the substances for which Stokes' Law, in its strict form, is violated.) Exposure to infra-red should therefore produce increased intensity near and beyond the violet edge of the phosphorescence band ; which is exactly what we have observed.

In the region where the absorption and emission spectra overlap, the effect will be more complicated. While the light in this region due to the ordinary luminescence band will diminish, there will be at the same time a temporarily increased emission due to the recombination of the unloaded ions that are shaken loose by the infra-red vibrations. A bright flash immediately after the exposure to infra-red followed by decay more rapid than the normal, is therefore to be expected in the intermediate region corresponding to Figs. 65 and 66.

The effect of the longer waves during excitation (Fig. 59) is unfortunately as hard to reconcile with this explanation of the phenomena as with that first suggested. It seems on the whole preferable to wait until additional data have been accumulated and other substances studied before attempting to develop the theoretical side of this extremely puzzling subject.

Variations of the Effect with the Wave-length of the Longer Waves.

In the case of several phosphorescent substances, including Sidot blende, the effect of rays of different wave-length in suppressing phosphorescence has been studied by a photographic method of Dahms. Our own results, obtained by an entirely different method, in general confirm the conclusions reached by Dahms in a very satisfactory way.

The arrangement of apparatus was similar to that used in our first experiments on the decay of phosphorescence.[1] A spark was used for excitation and a shutter was so arranged that the screen was exposed to the infra-red rays and the phosphoresence light allowed to fall on the slit of the spectrophotometer at the same instant that the excitation was brought to a close by short circuiting the spark. A Nernst glower was used as a source of infra-red rays. This was mounted in the place of the slit of a large mirror spectrometer with quartz prism.[2] The Sidot blende screen was covered with black paper except for a narrow rectangular region having

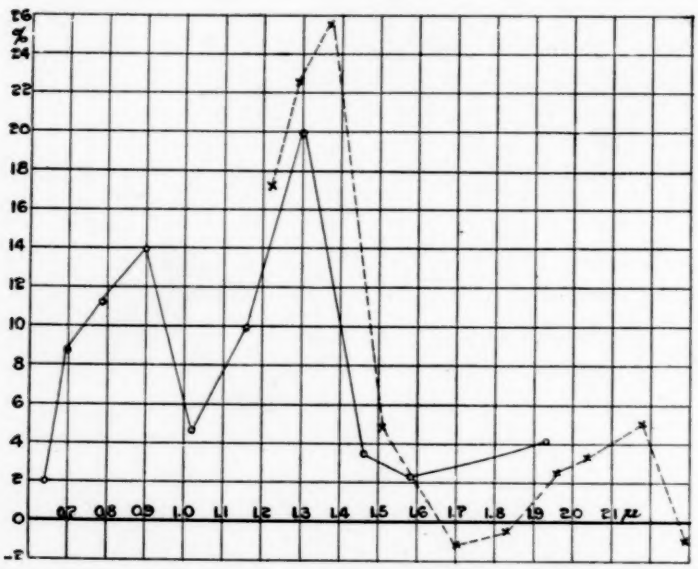

Fig. 68. Effect of infra-red rays of different wave-length. Ordinates represent the percentage diminution in the time of decay under the influence of infra-red.

about the same width as the Nernst glower. The adjustment of the spectrometer having been determined by observations in the visible spectrum, wave-lengths in the infra-red were computed from the angle of deviation. The effect of different rays from the Nernst glower was measured by the difference between the times required for the phosphorescence to fall from its initial intensity to a definite

[1] PHYSICAL REVIEW, Vol. 21, p. 247, 1905.

[2] Tests (by direct eye observation) with a rock salt prism showed that no effect was observable for wave-lengths longer than those transmitted by quartz.

final intensity with and without exposure to the rays to be tested. Each point on the curves shown in Fig. 68 is determined from the average of ten observations with infra-red and ten without, the observations being made alternately. The difference between the two, expressed as a fraction of the normal time of decay, has been plotted for the different wave-lengths used, which ranged from 0.6 μ to 2.3 μ. The observations refer to the region of maximum intensity in the phosphorescence spectrum (0.512 μ).

Referring to Curve I., Fig. 68, it will be seen that the effect of the longer waves is observable to some extent in the visible region. A maximum is reached at about 0.9 μ, followed by a minimum at about 1.0 μ and another maximum at 1.3 μ. From 1.2 μ on the observations were repeated under slightly different conditions the following day. (Curve II.) In this case the chief maximum appears to lie at 1.37 μ. The results are probably in all cases uncertain to the extent of 2 or 3 per cent., and errors are especially likely to be serious in regions where the effect is small. For this reason we cannot feel certain of the third maximum at 2.18 μ, although the probability is that it really exists. As far as any important effect is concerned, however, our results confirm the conclusion of Dahms that the action does not extend beyond 1.5 μ.

It can scarcely be doubted that absorption of the active rays is necessary before they can produce any effect upon phosphorescence. It seems probable, therefore, that Sidot blende possesses broad absorption bands with maxima not far from 0.9 μ and 1.37 μ. Experiments with other phosphorescent substances having ZnS as their base will be necessary to determine whether the absorption that determines this effect on phosporescence is characteristic of the solvent ZnS or of the dissolved metal causing luminescence. It is interesting to note, however, that in the absorption spectrum of sphalerite (ZnS) Coblentz has found evidence of bands at about 0.9 μ and 1.4 μ. While Coblentz's work does not indicate great absorption at these points it must be remembered that they fall in the most intense region of the spectrum of a Nernst glower, so that the total amount of energy absorbed might be very considerable.

SOME ELECTRICAL PROPERTIES OF SILICON.

BY FRANCES G. WICK.

I. THERMO-ELECTRIC BEHAVIOR OF METALLIC SILICON.

THE physical properties of metallic silicon, in so far as they have been investigated, show this substance to be of peculiar interest. The position of the element in the periodic system between the metals and non-metals may explain some of the deviations of its properties from those of the stronger metals. It resembles carbon, which stands next above it in the same group, in that it is a poor conductor of electricity and has a negative temperature coefficient of resistance.

The work here given upon the thermal electromotive force of silicon is the first of a series of observations upon the properties of this element which have been undertaken by the writer at the suggestion of Professors Nichols and Merritt. The silicon used is the most recent product of The Carborundum Company. It was cast in rods about 30 cm. long and 3 mm. in diameter by H. E. Heath,[1] of The General Electric Company, of whose kindness the author wishes to express her appreciation. The Carborundum Company state that their commercial product is at least 95 per cent. pure, the chief impurities being iron and aluminum.[2]

The extreme hardness and brittleness of silicon made the manipulation of it very difficult, the greatest problem encountered being that of making good electrical contact. An attempt was made to solder terminals to it, but this was impossible. The best connections were made by copper-plating the silicon. Even this method was not entirely satisfactory, since the copper plate pulls off easily.

[1] Mr. Heath, recognizing the large thermal effect of silicon in combination with different metals, has patented a thermo-couple, one member of which is to be silicon. Patent No. 824,015. June 19, 1906.

[2] Tone, Trans. Am. Electro. Chem. Soc., Vol. VII., 1905.

The method of determining the E.M.F. generated by a thermo-electric couple made of copper and silicon was as follows: The ends of a silicon rod were copper plated. Upon each end of this rod were placed two wires, one of copper and one of constantan. The electro-plating process was then continued until these wires were firmly fastened to the silicon rod by a bridge of copper. Pipe stems were used for insulation. Copper wires were soldered to the ends of these wires as shown in Fig. 1, making in all three sets of thermo-junctions, one of copper-silicon, and firmly plated to each end of the silicon rod, one of copper-constantan. The copper-

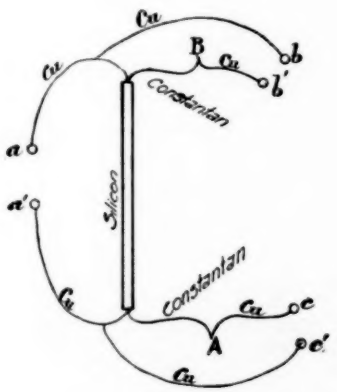

Fig. 1.

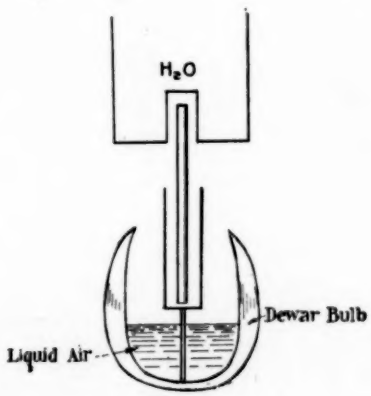

Fig. 2.

constantan couples were used for the determination of the temperature of the ends of the rod, the junctions not attached to the rod, A and B (Fig. 1), being kept at 0°.

The terminals of these thermo-elements aa', bb', cc' were dipped into mercury cups separated only by a thin layer of mica to avoid differences of temperature. Connections were thus easily made with potentiometer leads.

Measurements of thermal E.M.F. were made at temperatures ranging from about 350° to −190° C., one end of the rod being kept as near 0° as possible. Since the silicon rod is a good conductor of heat it was difficult to maintain the ends at a great temperature difference. For high temperatures the upper end of the rod was placed in a heating coil made of iron wire wrapped around a porcelain tube covered with asbestos. The lower end of the rod was

placed in a metal tube and this in a Dewar bulb containing a freezing mixture. For low temperature ranges the lower end of the rod was placed in a metal tube from which heavy copper wires projected into liquid air in a Dewar bulb, as shown in Fig. 2. By raising and lowering this tube temperatures varying from 0° to liquid air temperatures could be maintained. The upper end of the rod was kept at approximately 0° by means of a heating coil or by projecting upward into a tube surrounded by water of the required temperature.

It was often impossible to get steady conditions with one end of the rod exactly at 0° when the temperature of the other end was extremely high or low, hence a number of tests were carefully made covering the range of temperature through which the end of the rod varied from 0°. A curve was drawn showing the relation between the E.M.F. of the copper-silicon junction and a copper-constantan junction, one end of each being kept at 0°. By means of this curve the E.M.F. obtained was corrected to give that which would be obtained with one end of the rod at 0°.

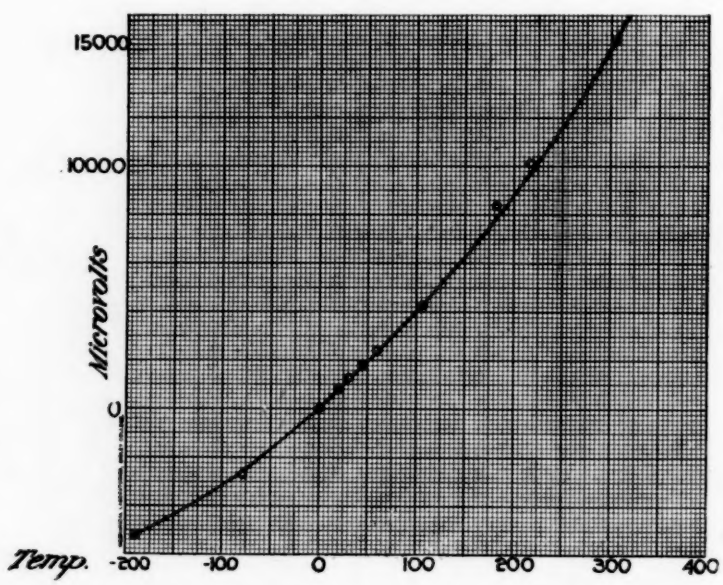

Fig. 3. Calibration curve of a copper constantan thermo-couple, one junction being kept at 0°.

The copper-constantan thermo-junctions on the ends of the rod were all made from the same spools of copper and constantan wire. A junction from these same spools had been made by Professor J. S. Shearer and calibrated from liquid air temperatures to the temperature of boiling benzophenone, the intermediate points being CO_2 and ether, water at temperatures from 0° to 100°, aniline and naphthalene. A similar junction made and calibrated through the same temperature range from — 190° to + 100° showed such agreement that the two calibration curves were identical.

TABLE I.

Rod No. 1. Length = 24.1 *cm. Average Diameter* = 3.24 *mm. E.M.F. in Microvolts.*

Copper-Constantan.		CuSi between (1) and (2).	CuSi between 0 and (2). From Calibration Curve.	CuSi between 0 and (1).	Temperature.
(1) Hot End.	(2) Cold End.				
541	100	−4,421	−950	−5,371	13.5°
842.5	247	−6,119	−2,367	−8,486	22.5
865	240	−6,187	−2,300	−8,487	22.5
840.5	254	−6,095.5	−2,450	−8,545.5	22.8
1,605.5	180	−14,135.5	−1,720	−15,855.5	40.5
1,611	174	−14,170	−1,670	−15,840	40.6
2,282.5	277	−19,531	−2,600	−22,131	56.4
2,283.5	275	−19,583.5	−2,550	−22,133.5	56.6
2,446	307	−20,874.5	−3,000	−23,874.5	59.8
2,456	311	−20,931	−3,050	−23,981	60.4
2,460	308	−20,949.5	−3,000	−23,949.5	60.5
2,466	317	−20,960	−3,100	−24,060	60.8
2,889	260	−25,217.5	−2,500	−27,717.5	70.3
5,713	528	−47,061	−5,170	−52,231	129.8
10,374.5	727	−80,105.5	−7,200	−87,305.5	215
12,020	738	−90,890	−7,320	−98,210	252
12,113.5	670	−92,381	−6,620	−99,001	255
16,666.5	693	−118,732.5	−6,850	−125,582.5	339
16,207	681	−119,145	−6,750	−125,895	340
16,846.5	648	−120,351	−6,400	−126,751	342
			CuSi between 0 and (1).	Computed CuSi between 0 and (2).	
617.5	−1,437	+19,218.5	−6,100	13,118.5	−36°
483.57	−2,408.55	+27,419.3	−4,740	22,679.3	−69
604.5	−2,590.25	+30,005.5	−6,350	23,655.5	−72
519.3	−3,694.8	+41,812.6	−4,980	36,832.6	−110.5
161.25	−4,814.5	+51,324.3	−1,500	49,824.3	−159
63.3	−5,340	+58,819.7	−570	58,249.7	−187

This calibration curve is given in Fig. 3. The high temperature points are those taken from the observations of Professor Shearer, the low temperature points being those taken by the author. After the tests on thermal E.M.F. of silicon were completed the silicon rod with its two attached copper-constantan junctions together with the previously calibrated copper-constantan junction was completely immersed in liquid air. Comparison of these three junctions showed no variation among them.

RESULTS.

The thermal E.M.F. between Cu and Si was thus obtained for three different rods. Tables I., II. and III. give the results. Table IV. gives the data used in drawing one of the calibration curves referred to above, from which the thermal E.M.F. which will be generated with one end of the rod at the given temperature and the other at 0° was computed. These curves are not reproduced here.

TABLE II.

Rod No. 3. *Length* = 21.2 *cm. Average Diameter* = 3.168 *mm. E.M.F in Microvolts.*

Copper-Constantan.		CuSi between (1) and (2).	CuSi between 0 and (2).	Computed CuSi between 0 and (1).	Temperature.
(1) Hot End.	(2) Cold End.				
140	0	−2,055	0	−2,055	4°
687.5	0	−7,721	0	−7,721	20.4
3,290	199	−31,005	−2,400	−33,405	79.2
4,753	318	−42,307	−3,550	−45,857	111
4,956	336	−43,865	−3,750	−47,615	114
4,965	331	−43,926	−3,670	−47,596	116
4,970	333	−43,910.5	−3,700	−47,610.5	116
7,988.5	557	−65,848	−6,220	−72,068	176
11,895	736	−91,835	−8,250	−100,085.5	250
14,247.5	877	−105,422.5	−9,780	−115,202.5	289
			CuSi between 0 and (1).	Computed CuSi between 0 and (2).	
439.7	−2,148.3	25,733	−4,700	21,033	−58°
262.36	−2,681.8	34,470	−2,920	31,550	−78.5
153.5	−3,732	41,076	−1,700	39,376	−113.5
1,543	−5,181	78,589	−15,000	63,589	−178.5
1,541	−5,181	78,537.5	−15,000	63,537.5	−178.5
300.4	−5,202	67,411	−2,950	64,461	−182.5

TABLE III.

Rod No. 4. Length = 30 cm. Average Diameter = 3.34 mm. E.M.F. in Microvolts.

Copper-Constantan.		CuSi between (1) and (2).	CuSi between 0 and (2).	Computed Cu Si between 0 and (1).	Temperature.
(1) Hot End.	(2) Cold End.				
104	0	−1,106	0	−1,106	3.3
560.5	0	−5,675.5	0	−5,675.5	15
768.5	0	−7,870	0	−7,870	18.5
754	0	−7,568	0	−7,568	19.3
1,395	0	−14,358.5	0	−14,358.5	35.5
1,632.5	60	−16,106.5	−600	−16,706.5	41
3,277.5	136	−31,635	−1,400	−33,035	79
4,403.5	0	−43,182	0	−43,182	103
8,780.5	60	−78,420	−600	−79,020	190
			CuSi between 0 and (1).	Computed CuSi between 0 and (2).	
205	−2,681	31,671	−2,100	29,571	−78.4
0	−5,204	60,442.5	0	60,442.5	−179

TABLE IV.

Calibration of Copper-Silicon Junction Against Copper-Constantan—one end of each being kept at 0°. E.M.F. in Microvolts.

Copper-Constantan.	Copper-Silicon.
560	−5,532.5
210	−1,996.5
190	−1,870
830	−7,950
81	−720

The direction of the current was found to be from Si to Cu through the hot junction. Silicon is therefore thermo-electrically negative with respect to Cu. Since Pb is also negative with respect to Cu the E.M.F. which would be generated between Pb and Si must be the difference between that generated by Cu-Si and Cu-Pb junctions at the given temperature.

This difference was computed by a table given by Dewar and Fleming.[1] The resulting curves for rods no. 1 and no. 2 are given in Fig. 4. The bismuth line from Dewar and Fleming's table has been put in for comparison. The original curve for thermal E.M.F. between Cu and Si at low temperatures is given in Fig. 5.

[1] Dewar & Fleming, Phil. Mag., Vol. 40, p. 95, 1895.

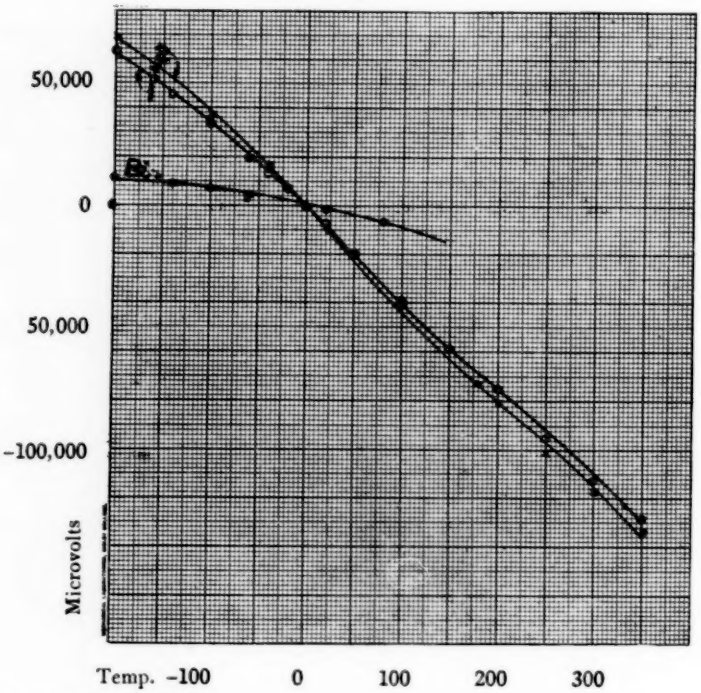

Fig. 4. Thermal E.M.F.
(1) Lead-silicon junction. Rod No. 1.
(2) Lead-silicon junction. Rod No. 2.
(*B*) Lead-bismuth junction.
Curves 1 and 2 were computed from Tables I. and II. and from copper-lead curve given by Dewar and Fleming.

It will be noticed that the thermal E.M.F. generated by a lead-silicon junction is very large. Another peculiarity about it is that the curve is not parabolic, being at least of the third degree. This double curvature may possibly be due to a large Thomson effect.

From curves drawn from the data given in Tables I. and II. the thermo-electric power of a silicon-copper junction was computed. This was done by finding the slope of these curves at intervals of 20°. The thermo-electric power line so found, given in Fig. 6, is not straight but has a maximum ordinate (negative) between 0° and 100° which diminishes as the temperature is raised or lowered.

The extremely large value of this thermal E.M.F. becomes evident by comparison with that produced by other metals in com-

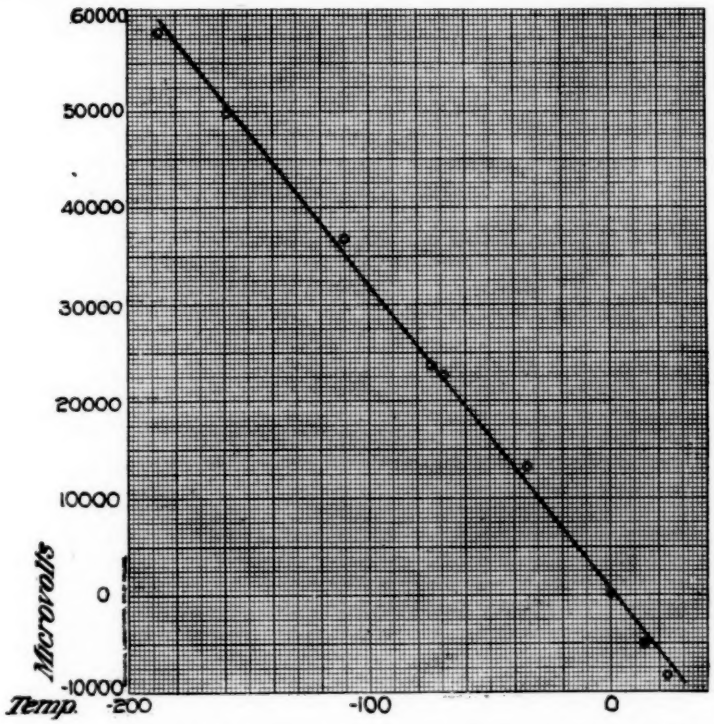

Fig. 5. Thermal E.M.F. between copper and silicon at low temperatures, one junction being kept at 0°.

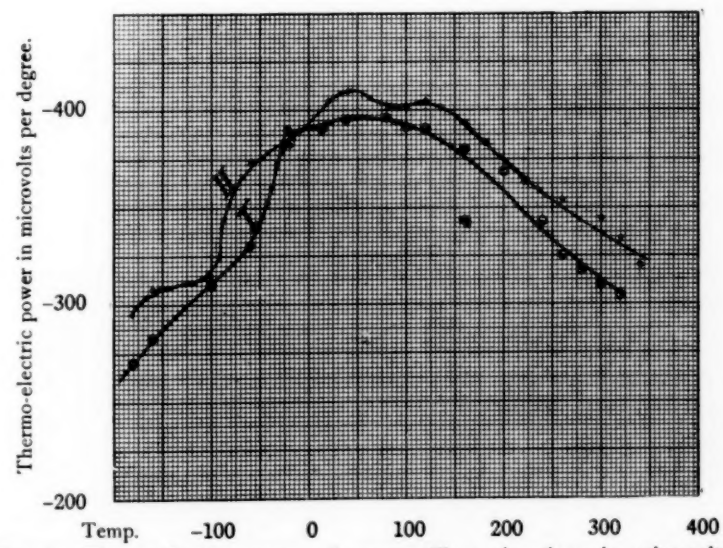

Fig. 6. Thermo-electric power of copper-silicon junctions in microvolts per degree centigrade.

Curve I. computed from measurements upon Rod No. 1.

Curve II. computed from measurements upon Rod No. 2.

bination with lead measured in microvolts per degree centigrade at a mean temperature of 20°C. At this temperature a lead-silicon junction gives a thermo-electric power of about − 400. The value for bismuth is − 89, for antimony + 26. Tellurium and selenium are comparable with silicon but of opposite sign, being + 502 and + 807 respectively.

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CONDENSATION NUCLEI OBTAINED FROM THE EVAPORATION OF FOG PARTICLES.[1]

By C. Barus.

1. *Standardization with Ions.*—A curious behavior appeared in an attempt to standardize the coronas of cloudy condensation by aid of the ions due to gamma rays penetrating the fog chamber. These were obtained from a sample of radium of strength 10,000 × and weighing 100 mg., sealed in an aluminum tube. The coronas were produced by successive exhaustions of the same value and the fogs were dissipated by compression, filtered air being introduced as soon as possible. The data obtained in the experiments showed an enormous initial loss. To obtain large coronas, the exhaustion to catch the ions was necessarily higher (drop of pressure $\delta p = 22.6$) than to catch the water nuclei resulting from the evaporation of fog particles ($\delta p = 17.1$); but this was allowed for.

The attempt to find the subsidence constant, S, fails; as for instance, if $s/30$ is the angular diameter of the coronas,

$s =$	4.7	3.3	2.0	1.0	4.4	3.0	1.8
$S =$	12.2	7.9	3.4		11.5	6.6	

showing a well marked progression of data. Similarly the attempt to find the initial nucleation n_0 fails, as a progression is here equally manifest. In other words, with the evaporation of the first fog (precipitated on ions) more than one half the nuclei are lost, whereas in subsequent evaporations, the behavior of the remaining nuclei is more like phosphorus nuclei, without evaporation losses.

That the discrepancy is in large measure due to the losses in the first evaporation will be seen if the second residue

$$(n \times 10^{-3} = 50.6)$$

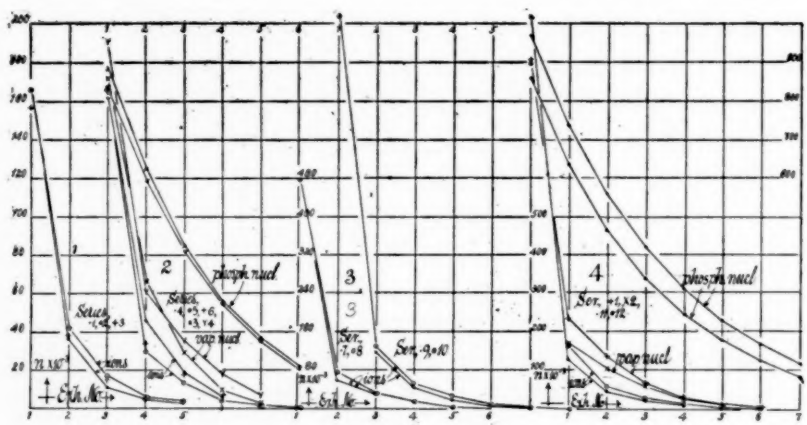
be taken as the initial number. The results are in thousands per cub. cm.

[1] Condensed from a report (now in preparation) to the Carnegie Institution of Washington.

	Nuclei Present.	Should be Present.	Nuclei Present.	Should be Present.
Ions.	$n = 76.9$	$n = 76.9$	$n = 76.9$	$n = 76.9$
After 1 evaporation.	22.3	50.6	18.3	50.6
" 2 evaporations.	7.7	8.0	5.8	6.2
" 3 "	1.7	.9	1.2	.4
" 4 "	.2	.1	.0	.0

2. *Systematic Data.* — Thus it appears that the water nuclei obtained by evaporating fog particles precipitated on ions vanish more rapidly, at least in the beginning, than may be accounted for as the combined result of the exhaustion applied and the subsidence. New results were therefore investigated by aid of the diffraction method [1] of two sources.

These are given in Figs. 1, 2, 3 and 4, where the ordinates show the number of nuclei caught in the successive identical exhaustions, and the abscissas the distributive number of the exhaustion



Figs. 1–4.

applied. Each exhaustion is followed by an evaporation of fog particles, whereby the residual water nuclei are produced for the next exhaustion in order.

In the first, second, and third series of experiments the exhaustion was somewhat above the condensation limit of air, so that the coronas do not vanish (Fig. 1). But as the vapor nuclei are rela-

[1] See Am. Journal of Science, XXIV., pp. 277–281, 1907.

tively few as compared with the ions, the initial fall of nucleation is well brought out. The exhaustion is here identical for ions and for water nuclei.

In series 4, 5, 6, the exhaustion for water nuclei is below the fog limit of air and the coronas vanish on successive exhaustion. It is necessary, therefore, to make the exhaustion for ions (only) above the condensation limit of air as otherwise too few would be caught. The observed march of data is however similar to the preceding experiments, as is shown in Fig. 2.

These results were now varied by bringing to bear stronger radiation obtained from an X-ray bulb placed at successively decreasing distances D from the fog chamber. In series 7 and 8, $D = 40$; in series 9 and 10, $D = 20$ cm.; and in series 11 and 12, $D = 12$ cm. (about) from the axis of the fog chamber. The large initial radiations drop off rapidly in the same way as in the preceding case. All the series are consistent, except the eleventh, in which the initial drop is too large compared with the others. It was customary to keep the exhaust cock open for five seconds, after which the filter cock was opened to dispel the fog, one minute being allowed between the exhaustions. The results are shown in detail in the figures together with similar data for the vapor nuclei of dust-free air and for phosphorus nuclei.

3. *Data for Vapor Nuclei.* — The figures contain similar data for the vapor nuclei of wet dust-free air. In series 1 and 2 large coronas or high nucleations are met with at the start, and they are compared in Fig. 4 with a corresponding case for ions. In series 3 and 4 lower initial nucleations are contained and these data are compared in Fig. 2 with the corresponding cases of ions and phosphorus nuclei. Corrections for subsidence should have been added to the graphs for ions and for vapor nuclei, but these are not large enough to modify them materially, so far as the figures go.

4. *Remarks on the Results.* — The graphs in Figs. 2 and 4 show unmistakably that the water nuclei obtained from the evaporation of fog particles precipitated on ions, vanish in the successive exhaustion faster than in the corresponding case with the vapor nuclei of dust-free air; while the water nuclei from fog particles precipitated on vapor nuclei vanish much faster than is the case for the corre-

sponding solutional nuclei obtained with phosphorus emanation. It is thus necessary to examine in detail the three more obvious causes for the decrease in the number of nuclei, which are as follows: (1) the exhaustions applied alike in all cases; (2) the subsidence of fog particles during the short time of their suspension, *i. e.*, between the exhaustion and the evaporation by influx of air; (3) the occurrence of electrical charge in the case of ionized nuclei whereby the charged water nuclei may be brought to coalescence.

Probably the best method of reaching a numerical result will consist in eliminating the effect of exhaustion and subsidence as was done for phosphorus nuclei, thus leaving the new losses of nuclei alone outstanding. If n_s' is the nucleation of the sth exhaustion,

$$n_s' = n_1 y^{s-1} \Pi(1 - S/s_{s-1}^2),$$

where y is the exhaustion ratio and the product $\Pi(1 - S/s_{s-1}^2)$, the correction for subsidence, the data obtained are such as apply for solutional nuclei produced by phosphorus; but they are throughout enormously in excess of the values n_s observed for vapor nuclei and for ions. Supposing that there is a second cause of dissipation with each exhaustion the equation may be written (abbreviating the products Π)

$$n_s' = n_1 y^{s-1} x^{s-1} \Pi$$

merely to get a numerical statement of the case. The values of x so found show a gradual increase, as the numbers of exhaustions increase or the nucleations decrease and the sizes of fog particles increase, so that the greatest dissipation of nuclei occurs during the first exhaustion.

If these values of x are summarized and constructed in terms of n, they also show that x is considerably in excess for vapor nuclei as compared with ions.

The best method of interpretating the above results is in terms of an equation of the form (if n_1 be the initial nucleation)

$$n_s = n_1 y^{s-1} x x' x'' \cdots \Pi,$$

where n_s is the nucleation of the sth exhaustion, y the exhaustion ratio, the product Π the subsidence correction and x, x', x'', etc., the successive coefficients showing the relative survival, x, or the

corresponding loss, $(1-x)$, of nuclei, accompanying each evapoartion of the fog particles. This equation asserts that the loss is different in the successive evaporations, which is actually the case in question.

So treated the results indicate the degree to which the first evaporation is preponderating and prove it to be more destructive, as the original number of ions is greater. Thus when $n = 160{,}000$, $(1-x)$ or 60 to 70 per cent. are lost during the first and only about $(1-x')$ or 20 per cent. during the second or subsequent evaporations. If $n = 900{,}000$ to $1{,}100{,}000$ (where the fog particles are very much smaller), the first destroys about 80 per cent., the second 40 per cent., the third 30 per cent. of the number which happen to be present just before the respective evaporation. Hence for large values of n the loss due to evaporation is appreciable throughout many repetitions.

The results, for fog articles precipitated upon the vapor nuclei of dust-free air are similar, but in no case does the coefficient of survival x increase after the first exhaustion, as was the case with ions. Contrasting the case of ions with the case for vapor nuclei, specifically, the coefficient of survival x is always decidedly smaller for ions in the first exhaustion than for vapor nuclei. The charged nuclei are therefore destroyed in greater number than uncharged nuclei by the evaporation of fog particles precipitated on them. When the number of nuclei is large (10^6), this is also true in subsequent evaporations, though the contrast is less marked.

Another question which comes up for settlement is this: Whether the fog particles which are represented by nuclei after evaporation are above a certain critical size, and those particles which vanish are below it. This is hardly probable because all the fog particles contribute to the same corona and because it implies an enormous inequality in the fog particles of the first exhaustion, seeing that 45 per cent. to 85 per cent. vanish in the different cases cited. These results for the diameters d of fog particles and the corresponding coefficients of survival x, x', etc., are constructed graphically in Fig. 5, *a*, *b*, for ions and in Fig. 5, *c*, *d*, for water nuclei.

Fig. 5, *a*, containing series 4 to 8 for small ionized nucleations (below $n = 500\ 000$), suggests that x may change abruptly when

$d = .0006$ cm.; while Fig. 5 *b*, for large ionized nucleations, 10^6, has the same appearance at $d = .0005$ cm. However, this is nothing more than the transition from the first to the second evaporation, the former being so much more efficient.

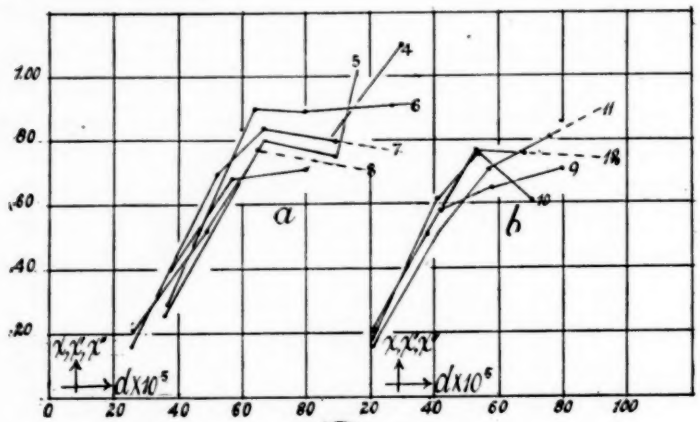


Fig. 5.

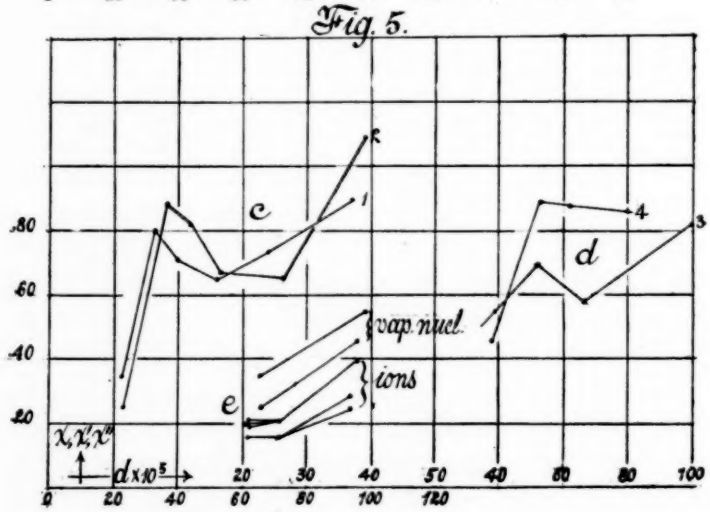


Fig. 5, *c* and *d*, for large and small nucleations of vapor nuclei has the same character. In *c* for instance there is an abrupt change below 40,000 nuclei. But the case is again one instancing the paramount importance of the first evaporation.

There is, however, no doubt of an outstanding effect due to the number or the size of the nuclei. The coefficient of survival x de-

creases as the number of nuclei increases, or better as their size diminishes. Thus if the comparison be restricted to the first evaporation, Fig. 5 *e*,

Ions:	$10^5\, d =$	38	37	37	26	26	21	22	21	21	cm.
	$10^2\, x =$	40	25	29	16	21	19	21	16	20	
Vapor nuclei:	$10^5\, d =$	39	38		23	23	cm.				
	$10^2\, x =$	55	46		25	25					

from which the increase of x with the size of the particles is put beyond question and the larger coefficient of survival for vapor nuclei as compared with ions is again apparent. Whether the peculiar features of the curve, Fig. 5 *c*, which reappears in each case, have a definite meaning must be left to conjecture; but in most of the curves, *a*, *b*, *c*, *d*, the occurrence of maximum x is in evidence.

6. *Loss of Nuclei Actually Due to Evaporation.* — It is finally to be shown that the peculiar loss of water nuclei resulting after evaporation of fog particles precipitated upon ions is due to this evaporation (or its equivalent) and not to the dissipation of the water nuclei in the lapse of time. It might be supposed for instance that water nuclei obtained from the fog condensed on the ions are smaller and therefore diffuse more rapidly than water nuclei obtained by other methods. If so, then if the time between the successive exhaustions is doubled, trebled, etc., the loss should be correspondingly increased. Data investigated on the above plan but containing the time interval, t, in minutes between the exhaustions, shows that the time effect is secondary. The interval t was varied from 1 to 6 minutes.

If the results are constructed in a figure like the above, the abscissa being the time in minutes, the ordinates showing the nucleation, the curves indicate a steady progression towards the right as the time interval increases, showing that the time losses although not necessarily absent are not of relevant importance. In fact the group of observations for one minute and six minute intervals, constructed in terms of the number of exhaustions (ignoring lapse of time), are virtually coincident. Again the curve for two minute intervals actually shows less loss (due to favorable exhaustion conditions) than the curve for one minute interval.

In one series of experiments, radium was left in place except during the exhaustion (for ions are efficient in presence of water nuclei). It was found that the water nuclei stored in this ionized field do not decay more rapidly than in ordinary dust free wet air.

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THE DIURNAL VARIATION OF THE SPONTANEOUS IONIZATION IN AIR IN CLOSED METALLIC VESSELS.

By T. Frederick McKeon.

Introduction.

AIR and other gases within closed metallic vessels are found to possess a slight conductivity even when not acted upon by an artificial ionizing agent. For a time it was thought that the presence of these free ions in the gas was due to an intrinsic property of the gas by which it was capable of ionizing itself. Recent investigations, however, have shown that some at least of these free ions must be attributed to the action of external agents. McLennan and Burton [1] measured the natural conductivity of the air in a large closed metal cylinder by means of a sensitive electrometer, and found that when the cylinder was completely surrounded with water the saturation current, or leak, through the vessel was greatly reduced. Rutherford and Cooke [2] observed that the rate of discharge of a sealed glass electroscope was diminished by placing a lead screen around the electroscope. Cooke [3] continued the investigation of the decrease of the rate of discharge in the electroscope, when surrounded by metal screens, and found that a thickness of 5 cm. of lead around the electroscope decreased the rate of discharge about 30 per cent., while further increase in thickness of the screen had no effect. An iron screen also diminished the rate of discharge to about the same extent as the lead.

A. Wood [4] has found that the diminution of the ionization by a given screen depended upon the material of the vessel. The ionization in a lead vessel surrounded by a lead screen was reduced 10

[1] Phys. Rev., V. 16, p. 185, 1903, and Phil. Mag., V. 5, p. 419, 1903.
[2] Amer. Phys. Soc., Dec., 1902.
[3] Phil. Mag., Vol. 6, p. 403, 1903.
[4] Phil. Mag., Vol. 9, p. 550, 1905.

per cent., while in an iron vessel it was reduced 24 per cent. Wood concludes from his experiments that the ionization observed in a closed vessel has a threefold origin. A part of it is due to an external penetrating radiation, part to a secondary radiation set up by it, while the remainder is due to an intrinsic radiation from the walls, altogether independent of the external radiation.

Patterson[1] examined the variation of the ionization of air with pressure in a large iron vessel of diameter 30 cm. and length 20 cm. The current between a central electrode and the cylinder was measured by means of a sensitive electrometer. He found that the saturation current was practically independent of the pressure for pressures greater than 300 mm. of mercury. Below a pressure of 80 mm. the current varied directly as the pressure. For air at atmospheric pressure the current was independent of the temperature up to 450° centigrade. With further increase of the temperature the current began to increase. The current was more rapid when the central electrode was charged negatively than when it was charged positively. This difference was ascribed to the production of positive ions at the surface of the iron vessel.

Strutt,[2] by means of an electroscope, observed that the ionization produced in a closed vessel varied with the material of the vessel. He found considerable differences, however, between different samples of the same material, and was inclined to conclude that the intrinsic radiation from the walls of the vessel was due to traces of radioactive impurities. A. Wood, working in the Cavendish Laboratory, repeated the experiments of Strutt, but failed to observe any differences in the ionization produced by different samples of the same material. The order of activity which he observed for the different materials was the same as that given by Strutt, with one exception. Similar experiments by McLennan and Burton, and Campbell confirmed the order obtained by these two observers. These experiments of McLennan and Burton, Wood, Strutt, and the others show that part of the spontaneous ionization in a closed vessel containing gas is due to the influence of the walls. H. L. Cooke has observed also that the ionization of the air in a brass electroscope could be

[1] Phil. Mag., Vol. 5, p. 680, 1903.
[2] Phil. Mag., Vol. 5, p. 680, 1903.

reduced to about a third of its usual value if the interior surface of the brass was carefully cleaned. By removing the surface of the brass he was able to reduce the ionization of the inclosed air from from 30 to 10 ions per c.c. per second. This is an important observation, and, as Rutherford has indicated, shows that a large proportion of the radio-activity observed in ordinary matter is due to a deposit of radio-active matter on the surface. It is well known that bodies which have been exposed in the presence of an emanation retain a residual activity, which takes some time to die out. The experiments of Bumstead [1] prove beyond a doubt that radium and thorium emanations exist in the atmosphere, and we may reasonably suppose that the exposed surface of matter, in consequence, will become coated with an invisible film of radio-active matter deposited from the atmosphere.

The experiments described in this paper were primarily undertaken with a view to ascertaining the modifications that should be introduced in the results of experiments such as were carried out by McLennan and Burton, if material was made use of which had been exposed to the atmosphere for a long time. To this end material was selected from a supply purchased some ten years previous to the carrying out of the experiments. This supply had been stored in the machine shop connected with the Department of Physics at the time of purchase, and the portion used had remained practically undisturbed up to the time of carrying out these experiments. The method followed was practically the same as that employed by McLennan and Burton, except that the cylinders used were considerably smaller than theirs. The results of the first few experiments showed surprising variations in the leak. These variations, which could not be accounted for by any of the known properties of the emanations of the radio-active bodies, were attributed to defects in experimental arrangements, and the method was abandoned in favor of a method, which will be described shortly, and which is in the main due to McLennan. However, the same obstacle to the accurate study of the radio-activity of the material employed was encountered. The leak again showed daily, and even hourly variations. A systematic study of these variations was now begun, and consid-

[1] Amer. Jour. of Science, Vol. 8, p. 1, 1904.

erable evidence had been obtained, which tended to show that the variations follow some law, when the writer received the recent article by Wood and Campbell,[1] and became aware that they had made the study of the variations, and had given a preliminary account of their results in a letter to *Nature*, as early as April, 1905. Since, however, the method of experimenting was different from that of Wood and Campbell, and the results obtained point to a different conclusion than that given in their recent account of their complete study of the phenomena, and, moreover, since all the data so far available upon which to base the law of the daily variation of the ionization in closed vessels had been obtained in only two places (Cambridge and St. Petersburg), it appeared that the problem justified a complete investigation. The work described in the following pages resolves itself into three parts: (1) an investigation of the leak between two cylinders of the same metal, (2) an investigation of the leak between cylinders of different metals, (3) and principally, a study of the daily variation of the leak between the cylinders.

APPARATUS AND CONNECTIONS.

In the experiments of McLennan and Burton, already referred to, the apparatus consisted of two cylinders, one placed within the other, and insulated from it. The outer cylinder was hermetically sealed and connected to earth. The inner was connected with one pair of quadrants of an electrometer. Rather large cylinders were used. The outer ones were 120 cm. in length, and 24 cm. in diameter, the inner cylinders were 110 cm. in length, and 19 cm. in diameter. In the experiments described in this paper much smaller cylinders were used; the outer ones being 60 cm. in length and 15 cm. in diameter, and the inner 55 cm. in length and 4 cm. in diameter. The arrangement of the apparatus, which differs from that of the authors named above in minor details only, is outlined in Fig. 1. A represents the outer cylinder, and B the inner cylinder between which the leak is to be measured. The cylinders are insulated from each other by blocks of paraffin and ebonite. A short brass rod, in metallic connection with B, passes through an ebonite plug fitted into A, and is protected by an earth-connected guard

[1] Phil. Mag., Feb., 1907.

ring. The brass rod projects a short distance within a tube also of brass; a hole in the top of the tube permits connection to be made between the brass rod and a fine copper wire stretched along the

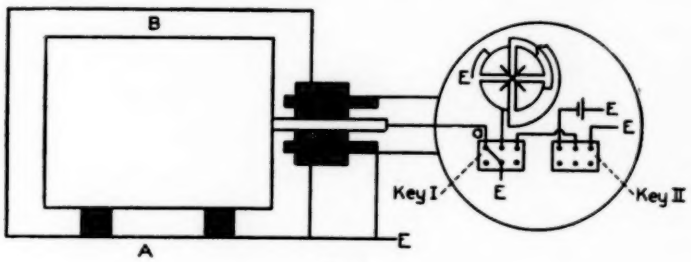

Fig. 1.

axis of the tube, and insulated from it by means of ebonite plugs. One end of this wire dipped into a mercury cup in a block of ebonite.

The electrometer used was of the Dolezalek type with amber insulation and adjustable quadrants. The needle was of silvered paper, and the suspension a quartz fiber dipped in a solution of calcium chloride to render it conducting. The needle was permanently connected with the negative pole of a Dolezalek-Nernst dry pile which kept its potential constant. The positive pole of the pile was connected to earth. The electrometer needle had a period of 60 seconds, and the damping was sufficient to make it dead beat. The zero position was fairly constant, the needle, except in one instance, not drifting through more than 2 cm. during the whole time of an experiment which was usually continued for more than four days. The sensibility did not vary appreciably during the same time.

The necessary connections were made with two simple trip keys which rested in mercury cups in a block of ebonite, and were worked mechanically, from a distance, by means of fine silk threads. A forward movement of key No. I., at the same time, broke the earth connection of the testing vessel, the earth connection of one pair of quadrants of the electrometer, and connected the vessel with the quadrants. When it was necessary to find the value of the scale readings in volts, a backward movement of key No. I. and a forward movement of key No. II. broke the earth connection of the

free quadrants, and connected them with the negative pole of a Carhart-Clark standard cell. The positive pole of the cell was earthed. The connections are given in outline in Fig. 1.

As very small potential differences had to be measured it was necessary to guard carefully against external electrostatic disturbances. The electrometer, the pile, which gave the charge to the needle, the keys for making connections, and the standard cell rested upon a wall shelf covered with tin-foil which was connected to earth. The electrometer, keys, etc., were covered with an earthed metallic screen made of wire, having twenty-five meshes to the square centimeter, covered with tin-foil. This screen proved most satisfactory, and protected completely against all external disturbances. The connecting wire between the testing vessel and the electrometer was inclosed in an earth-connected metallic tube.

METHOD OF WORKING.

After the outer cylinder had been adjusted upon two insulating blocks of ebonite, the inner cylinder and the insulating supports were placed in position within. A brass disk was inserted in the open end of the outer cylinder, and the joint thus made rendered air tight with paraffin wax. Connection was then made between the brass rod joined to the central cylinder and the wire, which dipped into the mercury cup *a*. The outer cylinder and the brass tube surrounding the connecting wire were next earthed. When the vessel was thoroughly sealed the free quadrants and the central cylinder were connected together, and their earth connections broken. The quadrants began at once to acquire a charge, which varied in intensity with the metals used. Because of the nature of the experiments, it was thought advisable to use a constant deflection method of measuring the current, and at the same time to avoid the complications which would arise from the use of resistance in parallel with the free quadrants. Under these circumstances the determination of the amount of charge to give the needle in order to obtain the maximum sensibility without causing the needle to deflect off the scale was a matter of several tests in almost every experiment. In case the current to be measured produced a deflection larger than could be measured on the scale, the sensibility

of the electrometer was reduced by decreasing the charge on the needle. The manner of determining this necessary charge was as follows: The central cylinder and free quadrants were connected together and insulated. The quadrants were then permitted to charge up until it was certain that the deflection would go beyond the limits of the scale, when the connection between the cylinder and quadrants was broken, and both were put to earth. The charge on the needle was then decreased, and the zero and sensibility redetermined. A number of tests of the constancy of these quantities was made after each change. It was found that if the needle was given a deflection a few times by connecting the quadrants to the standard cell, it settled down to a certain zero to which it always returned on further deflection in the same manner. Furthermore, it was found that all changes in the sensibility between observations taken within a few minutes of each other could be traced to imperfect conductivity of the quartz fiber, and could be entirely eliminated by redipping the fiber. When perfect constancy of zero and sensibility were attained, the cylinder and quadrants were once more connected together, and insulated. If the needle was again deflected beyond the limits of the scale the process was repeated, and this as often as was necessary, until the whole amount of deflection could be read. As ordinarily used the needle was kept at a difference of potential sufficient to give a deflection of 14 cm. on a scale at 120 cm. distance from the electrometer for a potential difference of one volt between the quadrants.

As a rule, an hour or more from the time the apparatus was sealed up and the quadrants first insulated, was spent in adjusting the charge on the needle so as to give the proper sensibility and finding the value of the scale readings in volts. Readings were begun immediately on insulating the quadrants, the spot of light from the mirror being read on a scale in the ordinary way. However, none of the readings taken before the final adjustment of the sensibility are given in this paper. For the first hour or two, from the beginning of the experiment, readings were taken every 3 or 7.5 minutes depending upon the rapidity with which the quadrants charged up. After that readings were taken at intervals of 12 or 15 minutes for 100 hours or more in each experiment.

It is evident that the method here outlined is open to some, though not serious, objections. First of all the method of rendering the needle conducting prevents the continuation of an experiment for any great length of time, and the necessity of regulating the sensibility of the electrometer makes it impossible to obtain the complete ionization curve from the time of sealing the apparatus.

RESULTS OF EXPERIMENTS.

In the experiments cylinders of lead, tin, aluminum and brass were used. Observations of the effect produced by combinations of these metals are set forth in the accompanying figures, where curves are drawn with the time expressed in hours of the day for abscissas and the deflection of the needle in arbitrary scale divisions for ordinates. It will be noticed that the variation of the ionization for all combinations of metals tried show three distinct characteristics. On connecting the central cylinder with the quadrants and insulating, the quadrants gradually acquire a charge which attains a maximum in a few hours, and then falls off, but never dies out altogether, or changes sign. This initial rise was observed by McLennan and Burton, but in their experiments the ionization did not fall off with time. When the experiments have been continued for 20 hours or more, the character of the phenomenon changes. At the end of this time the ionization has fallen to its lowest value, and the influence of two weak, but very definite sources of ionization, manifest themselves. The effect of the one is a progressive increase or decrease of the ionization, which is very evident when the experiment is continued for some days. Riding upon this progressive change in the ionization there is a change of periodic character, which has two maxima and two minima each 24 hours. Some evidence of the existence of this diurnal variation had been obtained already by different observers, but Wood and Campbell alone have pointed out that the daily period is twofold. A more complete understanding of what takes place will be gained by a detailed study of each curve.

ALUMINUM IN BRASS.

An inspection of the curves for aluminum within brass, Figs. 2 and 3, gives unmistakable evidence of these respective changes in

the ionization. The first curve, Fig. 2, shows the initial rise, which takes place on insulating the quadrants, and also the way the ionization falls off with time following this initial rise. A maximum is

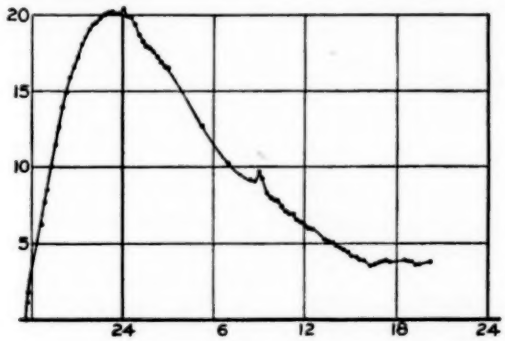

Fig. 2.

reached in about 6 hours, and in 22 hours the leak has fallen to a minimum. The subsequent periodic variations which take place in the leak, are already manifest in the latter part of this curve, but are made much more evident in the second curve, Fig. 3, which is plotted on a different scale. A period of 36 hours elapsed between

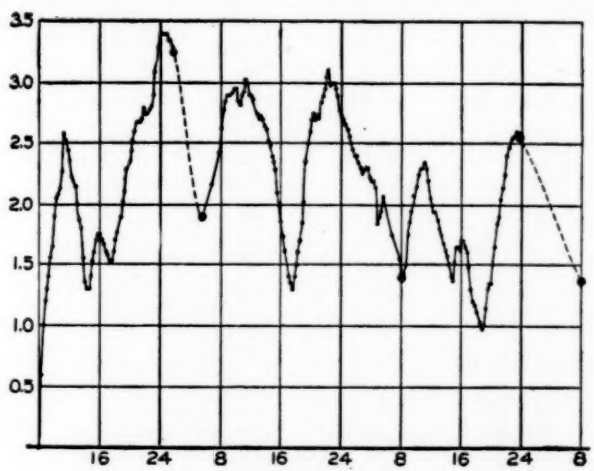

Fig. 3.

taking the observations plotted in the first curve and those plotted in the second, the quadrants in the meantime remaining insulated. This second curve shows a well-marked maximum for each day, at

Aluminum Cylinder within Brass Cylinder. Observations.

First Period. April 12, 1907. P. M.

Time.[1]	Scale Reading.	Amount of Deflection.
5.41	26.4	0.
5.44	25.25	1.15
5.47	24.65	1.75
5.50	24.5	1.9
5.55	23.9	2.5
6.41	20.05	6.35
6.54	18.7	7.7
7.	17.9	8.5
7.12	16.75	9.65
7.24	15.55	10.85
7.36	14.45	11.95
7.48	13.5	12.9
8.	12.6	13.8
8.12	11.78	14.62
8.24	10.8	15.6
8.36	10.25	16.15
8.48	9.55	16.85
9.	9.05	17.35
9.12	8.4	18.
9.24	7.96	18.44
9.36	7.64	18.76
9.48	7.28	19.12
10.	7.	19.4
10.12	6.95	19.45
10.24	6.84	19.56
10.36	6.48	19.92
10.48	6.38	20.02
11.	6.28	20.12
11.12	6.25	20.15
11.24	6.38	20.02
11.36	6.35	20.05
11.48	6.3	20.1
12.	6.36	20.4
April 13. A. M.		
12.12	6.42	19.98
12.24	6.5	19.9
12.36	6.7	19.7
12.48	7.3	19.1
1.	7.7	18.7
1.12	8.	18.4
1.24	8.3	18.1
1.36	8.5	17.9
1.48	8.52	17.88
2.	8.75	17.65
2.12	9.04	17.36
2.24	9.15	17.25
2.36	9.55	16.85
2.48	9.7	16.7
3.	9.8	16.6
5.20	13.7	12.7
6.58	16.15	10.25
7.54	16.9	9.5
8.24	17.2	9.2
8.36	17.25	9.15
8.48	17.43	9.06
9.	17.65	9.75
9.12	17.8	9.6
9.24	18.	8.4
9.36	18.18	8.22
9.48	18.4	8.
10.	18.51	7.89
10.12	18.65	7.75
10.24	18.88	7.52
10.36	18.95	7.45
10.48	19.15	7.25
11.	19.45	6.95
11.12	19.52	6.88
11.24	19.8	6.6
11.36	20.	6.4
11.48	20.	6.4
12.	20.2	6.2
P. M.		
12.12	20.4	6.
12.24	20.6	5.8
1.18	21.15	5.25
1.36	21.3	5.1
1.48	21.4	5.
2.	21.55	4.85
2.12	21.7	4.7
2.24	21.8	4.6
2.36	21.89	4.51
2.48	22.	4.4
3.	22.17	4.23
3.12	22.35	4.05

[1] As given by ordinary watch.

Aluminum Cylinder within Brass Cylinder. Observations.—Continued.

Time.	Scale Reading.	Amount of Deflection.
3.24	22.43	3.97
3.36	22.55	3.85
3.48	22.63	3.77
4.10	22.4	4.
4.30	22.18	4.22
4 45	22.09	4.33
5.	22.05	4.35
5.15	22.	4.4
5.35	22.06	4.34
6.30	22.	4.4
6.50	22.05	4.35
7.	22.05	4.35
7.12	22.3	4.1
7.30	22.25	4.15
8.15	22.1	4.3
Second period. April 15. A. M.		
8.15	27.3	+ .6
8.30	26.9	1.
8.45	26.7	1.2
9.	26.6	1.3
9.15	26.5	1.4
9.30	26.35	1.55
9.45	26.26	1.64
10.	26.	1.9
10.15	25.85	2.05
10.30	25.82	2.08
10.45	25.73	2.13
11.	25.63	2.27
11.15	25.33	2.57
11.30	25.38	2.52
11.45	25.46	2.44
12.	25.55	2.35
P. M.		
12.15	25.67	2.23
12.30	25.7	2.2
12.45	25.75	2.15
1.	25.9	2.
1.15	26.02	1.88
1.30	26.1	1.8
1.45	26.35	1.55
2.	26.55	1.35
2.15	26.5	1.3
2.30	26.6	1.3
2.45	26.5	1.4
3.	26.38	1.52
3.15	26.3	1.6
3.30	26.2	1.7
3.45	26.15	1.75
4.	26.15	1.75
4.15	26.21	1.69
4.30	26.24	1.66
4.45	26.3	1.6
5.	26.33	1.57
5.15	26.38	1.52
5.30	26.38	1.52
5.45	26.3	1.6
6.	26.2	1.7
6.15	26.13	1.77
6.45	26.	1.9
7.	25.86	2.04
7.15	25.72	2.18
7.30	25.6	2.3
7.45	25.55	2.35
8.	25.46	2.44
8.15	25.38	2.52
8.30	25.3	2.6
8.45	25.22	2.68
9.	25.22	2.68
9.15	25.22	2.68
9.30	25.2	2.7
9.45	25.1	2.8
10.	25.16	2.74
10.15	25.15	2.75
10.30	25.12	2.78
10.45	25.1	2.8
11.	25.	2.9
11.15	24.8	3.1
11.30	24.7	3.2
11.45	24.6	3.3
12.	24.5	3.4
April 16. A. M.		
12.15	24.5	3.4
12.30	24.5	3.4
12.45	24.5	3.4

Aluminum Cylinder within Brass Cylinder. Observations.—Continued.

April 16. A. M.

Time.	Scale Reading.	Amount of Deflection.
1.	24.55	3.35
1.15	24.55	3.35
1.30	24.6	3.3
1.45	24.65	3.25
5.25	26.	1.9
6.48	25.72	2.18
7.45	25.47	2.43
8.	25.28	2.62
8.15	25.13	2.77
8.30	25.05	2.85
8.45	25.	2.9
9.	25.	2.9
9.15	25.	2.9
9.30	24.98	2.92
9.45	24.95	2.95
10.	24.95	2.95
10.15	25.05	2.85
10.30	25.08	2.82
10.45	25.	2.9
11.	24.98	2.92
11.15	24.87	3.03
11.30	24.9	3.
11.45	25.	2.9
12.	25.01	2.89
12.15	25.03	2.87
12.45	25.17	2.73
P. M.		
1.	25.2	2.7
1.15	25.18	2.72
1.30	25.2	2.7
1.45	25.25	2.65
2.	25.28	2.62
2.15	25.33	2.57
2.30	25.41	2.49
2.45	25.5	2.4
3.	25.55	2.35
3.15	25.61	2.3
3.30	25.8	2.1
3.45	25.9	2.
4.	26.05	1.85
4.15	26.16	1.74
4.30	26.28	1.62
5.	26.5	1.4
5.15	26.55	1.35
5.30	26.6	1.3
5.45	26.5	1.4
6.	26.4	1.5
6.15	26.3	1.6
6.30	26.2	1.7
6.45	26.05	1.85
7.	25.88	2.02
7.15	25.54	2.36
7.30	25.4	2.5
7.45	25.3	2.6
8.	25.2	2.7
8.15	25.15	2.75
8.30	25.2	2.7
8.45	25.16	2.74
9.	25.18	2.72
9.15	25.05	2.85
9.30	25.	2.9
9.45	24.95	2.95
10.	24.84	3.06
10.15	24.86	3.14
10.30	24.91	2.99
10.45	24.9	3.
11.	24.9	3.
11.15	24.95	2.95
11.30	25.	2.9
11.45	25.12	2.78
12.	25.16	2.74
April 17. A. M.		
12.15	25.2	2.7
12.30	25.24	2.66
12.45	25.28	2.62
1.	25.34	2.56
1.15	25.4	2.5
1.30	25.44	2.46
1.45	25.5	2.4
2.	25.5	2.4
2.15	25.55	2.35
2.30	25.6	2.3
2.45	25.64	2.26
3.	25.61	2.29

Aluminum Cylinder within Brass Cylinder. Observations.—Continued.

Time.	Scale Reading.	Amount of Deflection.
3.15	25.6	2.3
3.30	25.61	2.29
3.45	25.67	2.23
4.	25.7	2.2
4.15	25.7	2.2
4.30	25.75	2.15
4.45	26.05	1.85
5.	26.	1.9
5.15	25.95	1.95
5.30	25.83	2.07
6.53	26.15	1.75
7.45	26.35	1.55
8.	26.5	1.4
8.15	26.48	1.42
8.30	26.4	1.5
8.45	26.15	1.75
9.	26.05	1.85
9.15	25.95	1.95
9.30	25.82	2.08
9.45	25.88	2.02
10.	25.75	2.15
10.15	25.65	2.25
10.30	25.6	2.3
10.45	25.6	2.3
11.	25.55	2.35
11.15	25.6	2.3
11.30	25.7	2.2
11.45	25.84	2.06
12.	25.9	2.
P. M.		
12.15	25.96	1.94
12.30	25.96	1.94
12.45	26.03	1.87
1.	26.1	1.8
1.15	26.15	1.75
1.30	26.22	1.68
1.45	26.28	1.62
2.	26.33	1.57
2.15	26.4	1.5
2.30	26.5	1.4
2.45	26.53	1.37
3.	26.38	1.52
3.15	26.25	1.65
3.30	26.25	1.65
3.45	26.28	1.62
4.	26.2	1.7
4.15	26.2	1.7
4.30	26.25	1.65
4.45	26.3	1.6
5.	26.43	1.47
5.15	26.6	1.3
5.30	26.7	1.2
5.45	26.73	1.17
5.55	26.78	1.12
6.25	26.85	1.02
6.45	26.93	.97
7.	26.9	1.
7.15	26.75	1.15
7.30	26.6	1.3
7.45	26.55	1.35
8.	26.55	1.35
8.15	26.4	1.5
8.30	26.25	1.65
8.45	26.05	1.85
9.	26.	1.9
9.15	25.84	2.06
9.30	25.75	2.15
9.45	25.65	2.25
10.	25.5	2.4
10.15	25.43	2.47
10.30	25.37	2.53
10.45	25.35	2.55
11.	25.34	2.56
11.15	25.3	2.6
11.30	25.3	2.6
11.35	25.35	2.55
April 18. A. M.		
8.	26.53	1.37

a time varying from 22.5 hours (10.30 P. M.) to 24 hours; second maximum about 11 hours; minimum between 17.25 hours (5.15

P. M.), and 18.5 hours (6.30 P. M.), and another between 5 hours and 5.5 hours. Hardly less interesting than these variations in the ionization is the difference in the amount of the charge on the quadrants on the first charging up, and that attained at any subsequent time during the continuation of an experiment. For the combination aluminum within brass the charge reached a maximum of 1.43 volts, and the highest value subsequently attained was only about .25 of a volt. The charge was negative. The observations from which the curves were drawn are given in the accompanying table of observations.

LEAD IN BRASS.

The first part of the curve for lead in brass, Fig. 4, presents an interesting variation from the form of the curve for other combinations of metals. Instead of falling off almost altogether and then

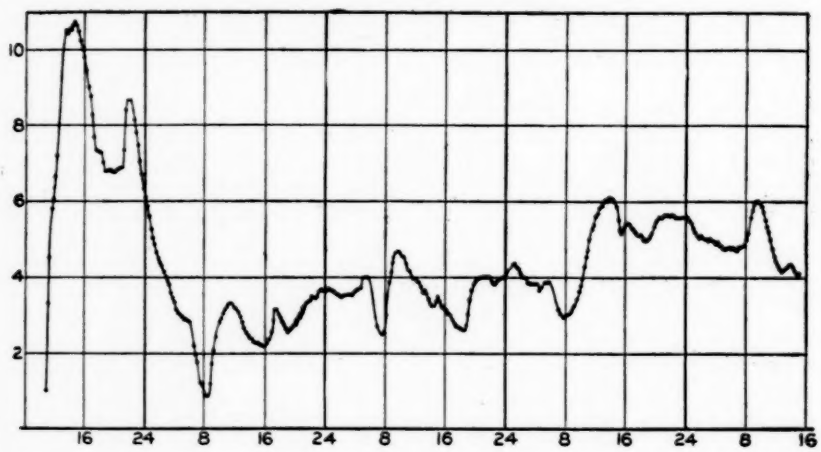

Fig. 4.

increasing, this curve shows that the leak decreased for from 4 to 5 hours, and then increased rapidly for a time, finally falling to a minimum, as is usual in 18 to 20 hours. It is worthy of note that this variation took place about the twenty-fourth hour, or the hour of midnight, at which time all the curves show a maximum. Besides this irregularity the curve shows two other striking peculiarities. One is the constancy of the minimum for each day at about the eighth hour, and the other, the so-called notched maximum, about midnight. If we disregard the first part of the curve and consider

only the portion given for complete days, we see that these midnight maxima are not the principal maxima as in the curves for aluminum in brass. The principal maximum in this curve comes at the time of the secondary in the former curve. The general outline of the two, however, are very like, and the variation is no doubt due to the increase in the amount of leak. As in the preceding curve, so here we find maxima for each day whose time of occurring varies from two to three hours. For lead in brass one variation of the maximum for successive days is from 22.5 h. to 24 h., and the other from 10 h. to 13.5 h. The minimum vary between 20 h. and 21 h. for one, and 7 h. and 9 h. for the other. If we consider the first part of the curve we have further evidence for the existence of the

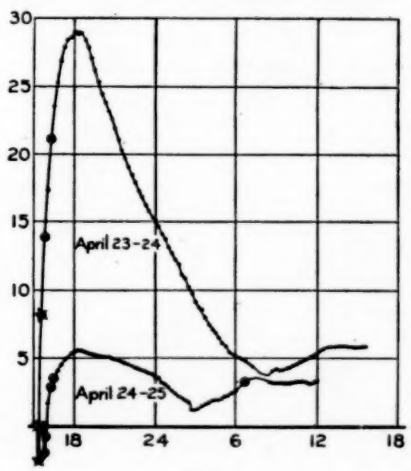

Fig. 5.

maximum between the twenty-second hour and the twenty-fourth. In this curve the progressive increase in the ionization is very evident, as it is in all the curves where one of the cylinders is of lead, and indicates that this steady increase is due to some property of the metal.

Lead in Lead.

The leak between a lead cylinder, and another of the same metal, was, in these experiments, so surprisingly great, that an effort was made to determine its source. Accordingly after the leak had fallen off, and had become comparatively constant, the inner cylinder

and the quadrants were disconnected and earthed. After about half an hour they were again insulated, and a new set of readings begun. The curves drawn for the two periods show the same general form. The rise in the second case, however, falls short of that attained in the first, and indicates that the ionization is due to a radio-active deposit on the surface of the metal, whose activity dies out with time. For both sets of readings the curves show that the maximum was reached in the same time, but in the second case the fall is less rapid. Since the time of fall in this case is almost coincident with the time of the principal maximum daily variation, we

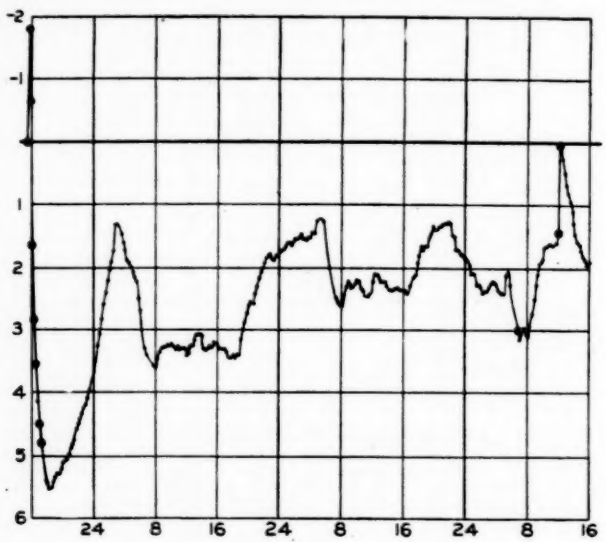

Fig. 6.

may attribute the retardation of the fall to whatever produces this variation. The observations from which this second curve was plotted, with subsequent observations are replotted in Fig. 6, in such a manner that the downward direction indicates a positive charge. The result of grounding the inner cylinder after the first twenty-four hours, and beginning a new set of observations is here clearly seen in a loss of definiteness in the periodic character of the curve. It is true, that we find maxima and minima at about the same hours at which they occurred in the curves previously given, but they are less clearly defined. If we consider full twenty-four

hour periods from one hour we find a maximum for each day for which the curve is drawn, at 22.5 h. Most evident of all, however, is the morning minimum, occurring as it does at 8 h. on three successive days. The afternoon fall though less evident is clearly defined and occurs as usual about the sixteenth or seventeenth hour. It must be pointed out, however, that two of the maxima observed do not come at a time at which maxima are usually observed, and that the two very great fluctuations observed at a time somewhat later than the usual time of the night maxima seem to be connected with weather conditions, for a storm was on at the time, and it has been invariably observed that a violent rain storm produces a marked increase in the deflection of the needle always in the direction indicating a negative charge.

Aluminum in Lead.

The observations from which this curve for aluminum in lead, Fig. 7, was drawn were taken after the central cylinder had been

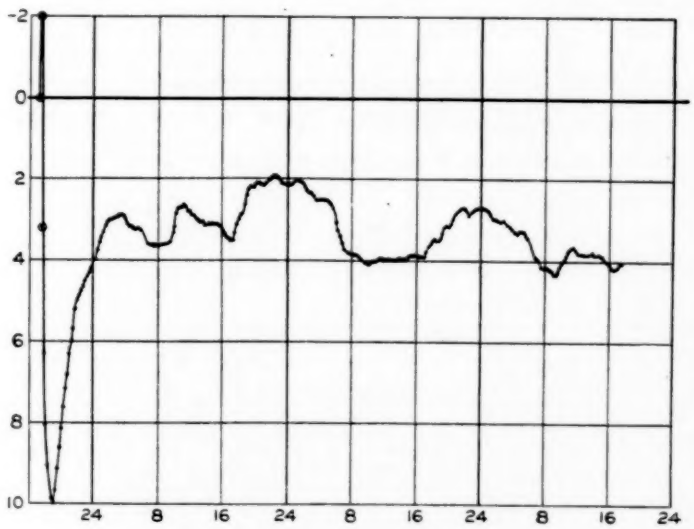

Fig. 7.

connected to the quadrants, and insulated for twenty-four hours. At the end of this time the quadrants were earthed and, after a brief interval, insulated again, and a new set of readings begun. The

curve for the first period is not given, as the first part of this curve corresponds with it in outline. The activity of this combination of metals was very great, the maximum deflection indicating a potential difference of over 2 volts. The curve is noticeable for the likeness it bears to the other curves where lead was the metal of the outer cylinder. To point out this likeness is of some importance since it indicates that the metal of the outer cylinder modifies, to some extent, the results obtained. As plotted the downward direction indicates the deflection corresponding to a positive charge and shows that there is a gradual increase of the charge from day to day. It will be noticed in these curves that the maximum and minimum are not preceded and followed by a rapid rising and falling of the curve, but that the maximum continues fairly level throughout the night, and the minimum throughout the day. Even so it is possible to recognize the usual maximum occurring from the twenty-second to the first hour, and a second maximum between 10 h. and 12 h. Minima occur between 16 h. and 18 h. and between 6 h and 9 h.

BRASS IN LEAD.

Observations with this combination of metals, Fig. 8, were continued for a somewhat longer time than in the preceding experiments with the hope that most convincing evidence of the regularity of the

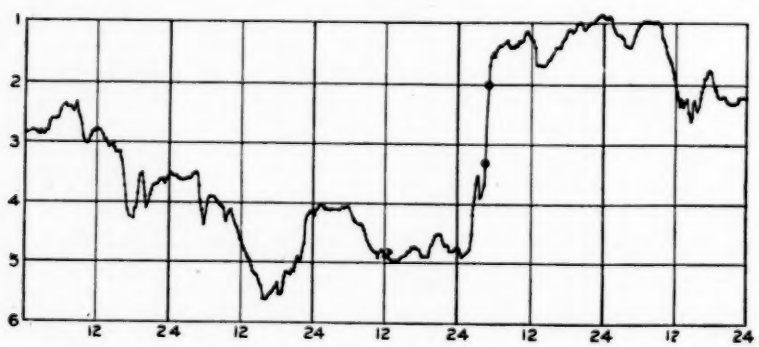

Fig. 8.

maxima and the minima would be obtained. However, the progressive change in the amount of ionization and in meteorological conditions, which undoubtedly have an influence, has broken up the

regularity somewhat, and on one day at least evidence of maxima and minima is not clearly defined. The curves, moreover, never indicate clear-cut maxima and minima quite satisfactorily when the deflection indicates a positive charge on the free quadrants. Except on one day when there was an unusually large variation which was coincident with a heavy rain storm accompanied by thunder and lightning, the time of occurrence of maxima and minima is in fair agreement with the results obtained by Wood and Campbell. Maxima occur at a time varying between 22 h. and 2 h. for the different days, and morning maxima varying between 7 h. and 9 h. The principal minima occur with great regularity between 14 h. and 18 h., and secondary minima may be recognized between 2 h. and 5 h. In general the results obtained with this combination of metals is in agreement with the results previously obtained, yet there are differences which suggest that the influences which bring about the variations are modified in their action by the nature of the metals used, and especially by the metal of the outer vessel. This supposition is strengthened by its general likeness with the other curves where the outer cylinder is of the same metal.

Tin in Tin.

This experiment was made merely for purposes of comparison with the results from other experiments, and to verify the order of activity of the metals, lead and tin, given by Strutt and others. This order is confirmed by the results obtained, lead having been found much more active than tin. A quantitative comparison was not attempted as it was next to impossible on account of the differences in experimental conditions.

Discussion of Results.

Some of the results obtained in these experiments are not in agreement with those obtained by McLennan and Burton. For example, they found, for all the metals tried, that if the cylinders

[1] At the end of this experiment it was found that the zero had changed considerably An effort was made to trace the cause. For this reason the apparatus was left intact for several hours. In about 12 hours a drift toward the original zero of 5 mm. was noted. Later the needle and quadrants were earthed then insulated, and a drift of 5 mm. noted in two hours. This would seem to indicate that the quartz fiber had suffered fatigue under the continued strain.

were of the same metal, the inner cylinder acquired a negative charge, whereas for the two metals, lead and tin, which I have tried, the inner cylinder acquired a positive charge. McLennan and Burton thought that the negative charge acquired by the cylinder resulted from a process in which an excess of positively charged corpuscles was expelled from its surface. At first sight it seems impossible to reconcile my results with those they have obtained, but if we consider that the discharge is due to some agent on the surfaces of the cylinders, or to a radiation from the surface of the metal itself, then the inconsistency may be explained away. In either case the amount of radiation should be proportional to the area of the surface of the cylinders. Hence if the cylinders are nearly of a size the amount of radiation from each will be about the same. On the other hand, if the cylinders are of quite different sizes then a much greater number of corpuscles will be shot off from one than from the other, and the cylinder from which the greater number is shot off will become negative with respect to the other. In McLennan's experiments the area of radiation does not greatly differ for the two cylinders, while in the experiments described in this paper the effective area was quite different. If now we suppose that the negative charge of the earth has a restraining influence on the escape of the positive corpuscles, the leak from the inner cylinder, which is insulated, will start first, and the two cylinders will act like a galvanic battery, with the inner cylinder as the negative pole and the air as a dielectric. The direction of the field thus created will have a retarding influence on the corpuscles from the outer cylinder, and more of them will be absorbed in their passage through the gas than if this field did not exist. If this absorption is sufficient to overcome the excess of corpuscles from the outer cylinder in McLennan's experiments, but not sufficient in the experiments herein described, then the two results are reconciled. Moreover, this interpretation not only reconciles the two results, it also enables us to explain why all the curves which ultimately indicate a positive charge show that at the start there was a deflection in the negative direction. The length of time of this negative deflection gives us a means of determining the strength of the retarding influence exercised by the earth's field, and by the leak between the cylinders. Furthermore,

the smallness of the negative charge measured by McLennan shows that the absorption was barely sufficient to overcome the excess of corpuscles from the outer cylinder. Further experiments will be made to test the soundness of this view.

To assign a cause for the periodicity of the ionization in a closed vessel, in the present state of our knowledge of the subject, is to present what must be considered more or less probable, and what must remain so until experiments have been made in widely different parts of the world. At best the explanations put forth, as in all cases where new ground is broken, must be looked upon as working hypotheses. So it is with the explanation offered by Wood and Campbell, and the one favored in this paper. Wood and Campbell trace a connection between the periodicity and the potential of the atmosphere, and give comparative ionization and potential curves for several consecutive months. These curves do, indeed, show a decided similarity, yet that Wood and Campbell themselves are not altogether satisfied that this seeming interdependence fully explains the phenomena is implied in their cursory reference to another possible cause.

One explanation of the phenomena that readily suggests itself is that the periodicity is due to the ionization which is known to be present in the atmosphere and indirectly to whatever produces this ionization.

Several observers have shown that radium and thorium emanations exist in the atmosphere, and Elster and Geitel have made a detailed examination of the effect of meteorological conditions on the amount of excited radio-activity to be derived from this source. A large number of observations were taken extending over a period of twelve months. They found that the amount of excited activity obtained was subject to great variations. Yet no evidence is given to show that these were periodic in character. No direct connection could be traced between the amount of ionization in the atmosphere and the amount of excited activity produced. More recently Dike[1] has obtained some evidence, which tends to show that there is a daily variation in the amount of radium emanation in the lower regions of the atmosphere. He found that the induced radio-activity depos-

[1] Terrestrial Magnetism, Vol. II., No. 3, p. 128.

ited on a negatively electrified surface in the Cavendish Laboratory has diurnal periods with a well-marked maximum at 1 A. M. Dike's observations, however, were continued only through six days. Similar diurnal variations in the amount of induced radioactivity have also been observed by Simpson[2] in Lapland.

In view of the fact that the theories already put forth to account for the periodic character of the ionization are not wholly convincing, it will not be out of place to consider another source of the ionization. O. W. Richardson[3] has pointed out that the connection between the periodicity in the ionization in closed vessels, and the variation in the intensity of the electric field near the earth's surface may be explained on the theory of conduction through gases if it is assumed that the ionization is caused by radiation from extra-terrestrial sources. The source of this radiation which Dr. Richardson suggests is the sun. Certain of the rays from the sun possess ionizing properties. These rays will be absorbed in passing through the atmosphere, and only the more penetrating will reach the earth. But in proportion as the rays are absorbed, ions are produced, hence the ions from this source will be more numerous in the upper regions of the atmosphere than nearer the earth. If, as Dr. Richardson does, we regard the earth and the upper atmosphere as two plane electrodes maintained at a constant difference of potential, we see that the ionization in the air near the upper atmosphere will be much more intense than near the earth, and hence the potential gradient will be least, for it has been found that where the ionization is to a large extent confined to the volume of air near one electrode, the potential gradient is least in its neighborhood and increases as the other electrode is approached. Thus any cause which brings about an increase in the intensity of the ionization in the upper air will increase the electric intensity near the surface of the earth.

The results of the experiments described in this paper are an indirect confirmation of this view in so far as they give evidence in favor of the source of the earth's electric field, upon which Richardson's conclusions are based. His theory of the origin of the earth's field is that it arises in rainy regions on account of the neg-

[1] Phil. Trans., 205, p. 61, 1906.
[2] Nature, April 26, 1906, p. 607.

atively charged rain conveying its charge to the earth, which thus becomes negatively charged. This leaves a high positive potential in the atmosphere immediately above the rainy region, which very rapidly distributes itself over the earth's surface by means of discharges in the upper regions of the atmosphere, where the pressure is low enough for ionization by collisions to occur. Owing to the high conductivity of the upper regions of the atmosphere, therefore, the potential will differ only to a relatively slight extent over different regions of the earth's surface; most of the fall of potential between the positive charge over the rainy region and any point on the earth's surface will occur in the badly conducting layer of air at a high pressure, which is comparatively close to the earth's surface. The main point in support of the above view of the origin of the earth's field, derived from the experiments herein described, is the observation, made repeatedly during the course of the experiments, that a rain storm was invariably accompanied by a rapid fluctuation of the charge on the free quadrants. On several occasions the fall of rain was preceded by lightning and thunder, but it was not until the rain began to fall that the rapid fluctuations of the charge took place. The connection between weather conditions and the unusual fluctuation of the charge on the quadrants has been pointed out in the discussion of each particular combination of metals, except for the first part of the experiment with the combination lead in lead, which was carried out while a heavy rain was falling. The observations taken during this period have not been plotted, as the fluctuation of the charge was accompanied by a change in the position of the zero, which rendered the value of the readings very uncertain.

Whatever be the source of the ionization, one thing is evident, the ionization in a closed vessel has a double daily period. Moreover, the uniformity in the time of occurrence of the respective maxima and minima in experiments made in so widely different parts of the world as Cambridge, St. Petersburg[1] and Washington makes the view that the variations are caused by radiation from the sun ionizing the air and thus bringing about a fluctuation in the earth's electric field, appear the most probable explanation of the phenomena.

[1] See Science Abstracts, 1904, No. 1580.

THE ABSORPTION OF HYDROGEN BY METALLIC FILMS.

BY WILL C. BAKER.

PROFESSOR SKINNER[1] has shown that when a discharge is sent, at low gas pressure, to a freshly polished cathode, hydrogen is liberated from the metal initially in the quantities required by Faraday's law for electrolytes. The proportionality between the mass of gas set free per second and the current soon diminishes (if the current be maintained), presumably as the available hydrogen in the surface layers is exhausted; for on standing in a hydrogen-free atmosphere the metal recovers its original power of giving off gas, probably through diffusion from the deeper layers. Heald,[2] in attempting to measure this absorbed gas by volatilizing the metal in a partial vacuum, concluded that the films thus condensed on the walls of the tube showed a measurable absorption of hydrogen. He states that even with quantities of active metal "too small to measure," a diminution of pressure was observable for an hour or more after the production of the film. Skinner[3] had already shown that the cathode in his experiments did not re-absorb the gas that had been liberated from it; but this was possibly due to the more ready absorption of hydrogen (probably atomic) from the interior of the metal. Thus it appeared quite possible — especially in view of Heald's observations — that a film of metal produced in a hydrogen-free atmosphere might show a measurable absorption on being exposed to hydrogen; also that it might be possible to determine the quantity of gas absorbed per gram of metal, if it were a volume effect; or the quantity of gas condensed per unit area if it were merely a surface phenomenon.

To decide these points metallic films of measurable mass were deposited by "spluttering" from a cathode, through a gas that had

[1] PHYS. REV., July, 1905.

[2] PHYS. REV., March, 1907.

[3] *Loc. cit.*

been carefully freed from hydrogen. The apparatus was then allowed to stand for an hour to permit it to cool from any heating arising from the deposition of the film; and finally, a known quantity of hydrogen was forced into the apparatus and the pressure measured from time to time. As the volume employed was less than one tenth of that used by Heald, and as weighable quantities of metal were used, the effect, if it existed under these conditions, would have been easily measurable. It was usually one minute after the introduction of the hydrogen that the first pressure reading was taken; but the pressure obtaining at the first contact of the film

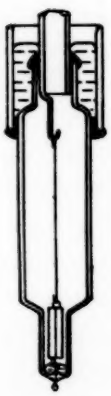

Fig. 1.

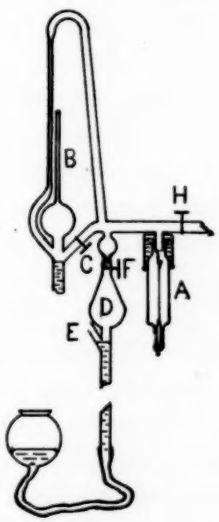

Fig. 2.

and gas could be approximately found from the volume of the apparatus, the pressure before the injection of the hydrogen, and the quantity of that gas used. Thus any absorption occurring in the first minute would have been detected. Cathodes of silver, iron and platinum were used. The two former are metals that gave large values in Heald's experiments. In no case was any absorption detected.

Figs. 1 and 2 give a diagrammatic representation of the experimental arrangements. In order to increase pressure changes the apparatus was kept as small as convenient, the main chamber with

attached gauge, etc., had a volume of about forty cubic centimeters. The cathode consisted of a fine wire seven centimeters long. This was hung from a glass hook as shown in Fig. 1 and was easily weighable before and after the experiment. It was slightly stretched by supporting at its lower end a small piece of capillary tube through which passed an aluminium[1] wire, making connection between the cathode and the fused-in platinum lead through a drop of mercury. This discharge chamber was attached to the rest of the apparatus by a sealing-wax joint, "drowned" in mercury; the latter serving to give it heat capacity, thus preventing the wax from softening during the discharge. The film had a superficial area of about forty square centimeters. The relation of this tube to the rest of the apparatus is shown in Fig. 2. *A* is the discharge chamber. *B* is a McLeod gauge. In order to enable readings to be made quickly, a by-pass with a tap, *C*, connected the main apparatus to the stem of the gauge at a point about a millimeter below the level of the capillary side tube. As this by-pass was about four millimeters diameter, the gauge quickly took up the pressure of the apparatus when the tap was open. In taking a reading the tap, *C*, was closed *just after* the mouth of the by-pass was covered by the rising mercury. The gauge then acted in the usual way. This arrangement gave complete satisfaction. The chamber, *D* (54.5 cc.), with tap *F*, served to give a definite volume of hydrogen and was connected through *E* to a half liter reservoir where that gas was stored over P_2O_5. A second McLeod gauge, also in connection with *D*, gave the pressure of this part of the apparatus. A fiducial mark was made about a centimeter above *F*, at a constriction in the tube, and the volume between this and *F* was kept full of mercury, forming a seal against hydrogen leaking into the discharge chamber from *D*. Knowing the volume of *D* from the side tube *E*, to *F*; and adjusting the pressure of the hydrogen filling it, a definite quantity of gas could be sent into the apparatus by first raising the mercury so as to close *E*; opening *F*, thus letting the mercury seal fall into *D*; then on continuing to raise the mercury to the fiducial mark the gas was forced into the main apparatus and the tap sealed as before. Between the tap *H*, which limited the

[1] Aluminium does not "splutter" in vacuo.

experimental volume in that direction, and the pump, were attached (1) a bulb containing the liquid alloy of sodium and potassium, (2) a spectrum tube an electrode of which served as the anode of the discharge chamber, and (3) a drying bulb with P_2O_5. The gauges "magnified" the pressure fifty times. All the taps were lubricated with a mixture of paraffin, vaseline and rubber according to Travers'[1] formula.

The experimental procedure was as follows: The discharge chamber and cathode were removed and a closed tube sealed on in their place. The tap *F* being open, the entire apparatus was exhausted by a water pump; then hydrogen[2] was let in through a tap not shown. This exhaustion and filling was repeated four or five times. The whole apparatus was next exhausted by the Toepler pump to a pressure of about one millimeter. The mercury was raised, filling *D*, and its level adjusted to the fiducial mark. *F* was then closed, and air admitted to the main apparatus. A current of air, entering through the stem of gauge *B* was maintained until the hydrogen had been swept out of the gauge and pump. The discharge chamber and weighed cathode were next put in place and the apparatus filled with nitrogen.[3] In the cases of iron and platinum the cathode was made red hot in a nitrogen atmosphere by running the discharge, at a pressure of six one hundredths of a millimeter; and the apparatus was filled with nitrogen four times more, exhausting each time to one millimeter. This gas was allowed to stand for twenty or twenty-two hours in contact with P_2O_5. After drying, the gas was purified from any remaining hydrogen by running the NaK bulb with the alloy as cathode, until the spectrum of hydrogen had entirely disappeared. A Browning direct vision spectroscope was used. After purification, the film was deposited, let cool for an hour, the hydrogen injected and the readings made. A few hours later the ratio of the volume of *D* to the experimental volume was determined by measuring the increase in pressure produced in the apparatus by the introduction of a definite quantity of gas. This ratio varied from experiment to experiment due to the

[1] The Study of Gases.

[2] From Zn and HCl, dried by bubbling through strong H_2SO_4.

[3] Prepared as recommended by Travers (loc. cit.) by drawing air from outside the building, through strong NH_3, then over red hot copper turnings, and finally through two wash bottles of concentrated H_2SO_4 to remove moisture and excess of ammonia.

fact that the sealing-wax joint was seldom twice in exactly the same place.

On account of the small volume employed the well-known effect of the lowering of the gas pressure accompanying discharge was especially prominent during the deposition of the film. In the case of iron five hours were required in this process. Also the NaK alloy absorbs nitrogen as well as hydrogen. This would soon increase the vacuum until the discharge would not pass were there not some means of feeding gas back into the tube. To overcome this the valve chamber of the pump was utilized. During the final drying the gas was left at a pressure of about a half a millimeter; the mercury having been turned completely through the pump leaving no gas in the valve chamber *X* (Fig. 3). After drying and purifying, the apparatus was pumped down to the required pressure but the excess of gas was *not turned out of the pump;* it was allowed to remain in the chamber *X*, being kept there by the traps at *Y* and *Z*. If now the mercury in the main stem were lowered below the level of the mouth of the tube *Y*, and if more mercury were poured into the fixed reservoir at *R* until its surface was less than the barometric height below the bend above the valve chamber, large drops would fall on top of the open valve and slipping down would enclose gas in the tube *Y* and force it over into the pump head and so into the apparatus. This process could be stopped by lowering the mercury in *R*. In this way dried and purified gas could be returned to the discharge tube at will.

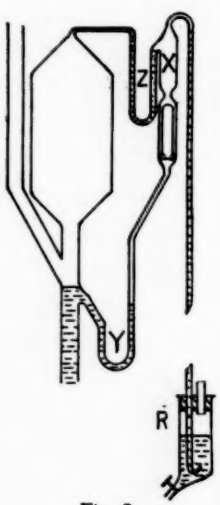

Fig. 3.

TYPICAL MEASUREMENTS. IRON.

Cathode wire well cleaned with sand paper. Heated to bright redness in nitrogen at 4/50 mm. Apparatus refilled four times.

Film deposited at 4/50 mm. after drying and purifying gas. Film a light brown at edges but a black mirror in body of deposit.

Mass of wire before depositing	0.0280 gms.
" " " after "	0.0260 "
" " film deposited	0.0020 gms.

54.5 cc. hydrogen admitted to discharge chamber at		32.5 fiftieths of mm.
Gas in discharge chamber before admission of hydrogen at		2.4 " " "
Hydrogen injected at 11 hrs. 06 min. A. M.		
Pressure observed at 11 " 07 "		45.2 fiftieths of mm.
" 08 "		45.2 " " "
" 10 "		45.2 " " "
" 14 "		45.2 " " "
" 18 "		45.1 " " "
" 22 "		45.2 " " "
" 27 "		45.2 " " "
" 38 "		45.2 " " "
" 45 "		45.2 " " "
1 hr. 15 " P. M.		45.0 " " "
Ratio of volume *D* to discharge chamber, etc., 1.29.		
Pressure immediately after injection of hydrogen, calculated,		44.4 " " "

SILVER.

Wire cleaned with sand paper. Film deposited at 3/50 mm. after drying and purifying gas. Film a bright metallic mirror.

Mass of wire before depositing		0.0756 gms.
" " " after "		0.0744 "
" " film deposited		0.0012 gms.
54.4cc. hydrogen admitted at		44.8 fiftieths of mm.
Gas in discharge chamber before admission of hydrogen at		2.4 " " "
Hydrogen injected at 9 hrs. 54 min. A. M.		
Pressure observed at " 55 "		61.0 fiftieths of mm.
" 56 "		61.0 " " "
" 58 "		60.8 " " "
10 " 00 "		61.0 " " "
" 03 "		60.8 " " "
" 06 "		60.8 " " "
" 10 "		60.9 " " "
" 14 "		60.9 " " "
" 19 "		60.9 " " "
" 25 "		60.8 " " "
" 41 "		60.9 " " "
11 " 20 "		60.9 " " "
1 hr. 04 " P. M.		60.8 " " "
2 hrs. 35 "		60.8 " " "
9 " 00 " A. M. (next day)		61.8 " " "
Ratio of volume of *D* to discharge chamber, etc., 1.29.		
Pressure immediately after injection of hydrogen, calculated		60.2 " " "

PLATINUM.

Cathode boiled in strong nitric acid to remove occluded hydrogen,[1] washed, and dried in filter paper. After first filling with nitrogen the wire was raised to a bright red heat for one minute. During the deposition of the film the current was run to the wire for five seconds then to the NaK alloy for the next five seconds, then to the wire again and so on using the alloy and wire alternately, five seconds each, during the entire period of formation of the film. No trace of the hydrogen spectrum could be detected under this treatment. In other experiments it was found that after the gas had been purified, one could just detect the hydrogen lines when the discharge had run twenty seconds continuously. The film was a mirror, slightly dull owing to the deposition of larger particles during the heating after first filling. Film deposited at 3/50 mm.

Mass of wire before deposit	0.0261 gms.
" " " after "	0.0243 "
" " film deposited	0.0018 gms.
54.5 cc. hydrogen admitted at	38.2 fiftieths of mm.
Gas in discharge chamber before admission of hydrogen at	1.2 " " "
Hydrogen injected at 11 hrs. 20 min. A. M.	
Pressure observed at " 21 "	51.7 fiftieths of mm.
" 23 "	51.7 " " "
" 25 "	51.7 " " "
" 29 "	51.7 " " "
" 34 "	51.7 " " "
" 40 "	51.7 " " "
" 45 "	51.7 " " "
12 " 50 "	51.7 " " "
1 hr. 45 " P. M.	51.7 " " "
Ratio of volume D to discharge chamber, etc., 1.31.	
Pressure immediately after injection of hydrogen, calculated,	51.3 " " "

The measurements given above indicate that cold metallic films, resulting from cathode deposition, across a hydrogen-free space, do not show a rapid absorption of hydrogen from the molecular state, at least within the limits of accuracy of the experiments recorded in this note.

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[1] Wilson, H. A., Phil. Trans. Roy. Soc., *A*, Vol. 202, p. 253.

SOME PHYSICAL PROPERTIES OF CURRENT BEARING MATTER; IV. FRICTION.[1]

By Paul R. Heyl.

THIS article describes some experiments on the effect of a current upon the friction between a solid and a liquid, the liquid being mercury and the solid either carbon or iron.

For iron, with a current density of about 80 amperes per square centimeter, there is no change in friction as great as one per cent. For carbon, with about the same current density, while there is an apparent decrease of about 14 per cent. with the current, this is entirely accounted for by the accompanying heating effect.

The best method of determining the friction between a solid and liquid is to observe the damping of torsional vibrations when the solid swings in the liquid. If the speed is at all times sufficiently slow, we may assume that the friction is proportional to the speed. On this assumption we have a constant damping factor, or ratio of two successive amplitudes, and the friction is proportional to the Napierian logarithm of this ratio.

When the liquid wets the solid we have, on account of the adhesion of the contact surface, simply the viscosity of the liquid upon itself; but where this is not the case we have in addition the friction at the liquid-solid surface. As already stated, the liquid used was mercury. The metals which are wet by mercury dissolve in it, and we may therefore expect a gradual change in the liquid viscosity where such metals are employed. For this reason, carbon and iron, which do not dissolve in mercury, were chosen. With these substances, the friction, although complex, may be depended upon to be constant.

The form of apparatus used is shown in Fig. 1. A rectangle *AA* of heavy copper wire carried the short rods *BB* of iron or carbon

[1] Earlier articles appeared in Physical Review, XIX., 4 and XXI., 3.

which dipped into the mercury cups *CC*. A current introduced by one of these cups will pass through both sides of the rectangle and leave by the other cup. Several heavy weights *D* served to increase the time of swing to about 25 seconds. The whole arrangement was suspended by a wire *E* some two meters long, and enclosed in a box with a glass front, the wire *E* passing out by a hole in the top of the box. This wire carried a light pointer which moved over a graduated circle on the top of the box. This circle was printed on cardboard, divided to half degrees, and as its diameter was some 20 cm. it was easily read with a lens to tenths of a degree.

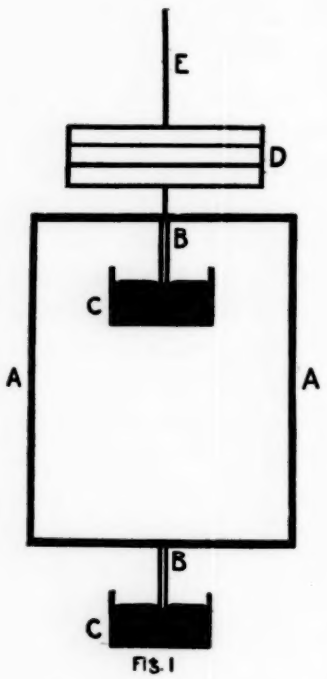

FIG. 1

To get as high a current density as possible the rods *BB* were small in diameter, about 3 mm., and dipped very slightly into the mercury. The surface of contact in each cup was about 0.075 sq. cm. With a current of 6 amperes this gave a current density of about 80 amperes per sq. cm. at each point of friction. More than this could not be used without danger of forming an arc.

It was soon found that the ratio of successive amplitudes was not constant, but suffered a progressive change as the amplitude decreased. Consequently the following procedure was adopted:

The pointer was drawn aside to a certain mark and held there until all swinging of the apparatus had ceased. It was then released and the next three consecutive turning points recorded. From these was calculated the ratio of two successive amplitudes. The first swing was about 60°.

The current was then turned on, and the operations repeated, starting the pointer from the same point. The experiments were thus continued alternately with and without a current.

When carbon rods were used their relatively high resistance

caused a considerable development of heat. They were pieces of electric light carbon, and after a little time became too hot to be touched by the finger. On account of the large amount of mercury in the cups the temperature of the mercury never rose above 35° as measured by a thermometer with a small bulb immersed in the mercury close to the rod. There is no doubt, however, that a very thin film of mercury next the rod was heated more intensely than this.

The effect of the heat upon the viscosity of the mercury may be considered to be eliminated by the alternate method of observing; for the mercury heated by experiment with current had not time to cool more than two or three degrees during the following experiment without the current, and the average temperature of the two sets of experiments was about the same.

We cannot, however, neglect the effect of the heat at the liquid-solid surface. A special set of experiments was made to determine about how much the heating effect might amount to.

The results are given in a condensed form.

Iron-mercury. Current Density, 80 Amperes Per Sq. Cm.

	Current.	No Current.
Mean ratio of successive amplitudes (40 values)	0.9245	0.9239
Average departure from mean	0.005	0.006
Napierian logarithms of ratios	−0.0786	−0.0792

Difference, about 6 parts in 800.

Carbon-mercury. Current Density, the same.

	Current.	No Current.
Mean value of 40 ratios	0.952	0.946
Average departure from mean	0.003	0.004
Napierian logarithms of ratios	−0.0488	−0.0556

Difference, about 7 parts in 50.

To test the heating effect 15 ratios were measured with no current, the mercury being about 22°. The average ratio was 0.9484 with an average departure of 0.001. The current was then allowed to flow for half an hour, raising the mercury to about 52°. Ratios were measured with the mercury at this temperature, interrupting the current just long enough to measure the two swings necessary for each ratio, and restoring it as soon as that measurement was over. In this way the average temperature of the mercury was kept at about 54°.

Twelve ratios thus measured gave a mean of 0.9613 with an average departure of 0.002. It is thus evident that the effect of the heat at the liquid-solid surface is ample to account for the change observed with carbon, the change here being some 27 per cent. for a rise of about 32°. This is confirmed by the absence of any effect of current upon friction in the case of iron, where the heating effect was negligible.

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